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HIGH DENSITY JET FUEL SUPPLY AND SPECIFICATIONS

Carl M. Smits

J & A Associates  
18200 West Highway 72  
Golden, Colorado 80401



January 1986

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Teresa A Planeaux

TERESA A. PLANEAUX  
Fuels Branch  
Fuels and Lubrication Division  
Aero Propulsion Laboratory

Arthur V. Churchill

ARTHUR V. CHURCHILL  
Chief, Fuels Branch  
Fuels and Lubrication Division  
Aero Propulsion Laboratory

FOR THE COMMANDER

Benito P. Botteri

BENITO P. BOTTERI  
Assistant Chief  
Fuels and Lubrication Division  
Aero Propulsion Laboratory

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## PREFACE

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The Technical Representatives for this subcontract were Mr. Ross Luce and Mr. Arthur Levy of Battelle, and the Government Focal Point consisted of C. L. Delaney and Dr. H. R. Lander of the Aero Propulsion Laboratory.

This report covers only the subcontract work undertaken by J & A Associates during the subcontract interval of August, 1985 through January 1986.



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## Section I

### Results

In order to significantly increase the range of military aircraft, the U. S. Air Force is contemplating a changeover to higher density jet fuels. This study examined the potential availability of such fuels and provided analytical data obtained on representative samples. Results obtained are as follows:

- Present production of refinery streams that would meet tentative high-density specs is approximately 150,000 bbl/day or about 50% of military usage.
- These high-density fuel candidates are rarely sold as jet fuel due to their low smoke point, usually being blended off or sold as diesel. Relaxing smoke point specs would make them immediately available.
- All U.S. Hydrocrackers have the potential to produce approximately 850,000 bbl/day of high-density fuel, or 85% of total U.S. kerosene type jet fuel consumption. Their production would be primarily at the expense of gasoline production.
- Straight-run cuts from naphthenic crudes can provide as much as 360,000 bbl/day of high density fuel. Most of this material would require some hydrotreating. This production would be at the expense of diesel (#2 fuel oil) production.
- Availability of high density fuels over the long term is excellent. Hydrocracker feed is primarily FCC light cycle oil, which is produced in the U.S. at over 1 MM bbl/day, and U. S. naphthenic crude oils have a higher reserves to production ratio than normal crudes.
- With one exception, all the high density fuels analyzed have low smoke points which may mean:
  - (1) Less than ideal engine combustion characteristics.
  - (2) Greater than desired visibility of aircraft.
- The tentative JP-8X (high density JP-8) specs appear to be attainable. Tentative JP-11 specs appear to not be attainable using the HD jet sources examined here.

## Section II

### Introduction

High-density kerosene type jet fuels are being examined by the U. S. Air Force in order to increase the range of volumetrically limited military aircraft. Present JP-8 fuels range from 37 to 51 °API (0.775 - 0.840 g/cc) and contain approximately 124,000 Btu/gal (net). Target high-density fuels of less than 37°API (0.84 g/cc) would have net heating values greater than 130,000 Btu/gal and could extend aircraft range as much as 15%<sup>(1)</sup>.

Fuel density is dependent upon molecular size and molecular type. The molecular size of kerosene type jet fuel is restricted on the heavy end by low temperature requirements (viscosity, freeze point) so the fuel will flow at high altitude and during winter. Molecular size on the low end is restricted by engine requirements for volatility (flash point, vapor pressure). Therefore, for present jet engines, the molecular size or boiling range of the fuel cannot be significantly altered to increase fuel density.

The second way to increase fuel density is to alter the molecular type. Present kerosene type fuels are primarily composed of paraffins, preferably isoparaffins. These molecules are high in hydrogen ( $C_nH_{2n+2}$ ) and burn cleanly. But they are relatively spacious molecules and result in a low-density fuel. Present fuels also contain some cycloparaffins ( $C_nH_{2n}$ ) and aromatics ( $C_nH_n$ ) which are much more compact molecules and contribute to a more dense fuel. Generally, the aromatics, which are the densest components, are considered to be undesirable, because, in present engines, they do not burn cleanly. Therefore, present fuels have limits on total aromatics content, on naphthalene in particular, and on smoke point, luminometer number, or hydrogen content, all of which are indicative of aromatic content.

Since greatly increasing the aromatic content of jet fuels may cause problems in present engines, the preferable approach is to increase the cycloparaffin (naphthene) content. Naphthenes burn more cleanly than aromatics, containing more hydrogen, and they have better low temperature properties than aromatics. Therefore, most efforts to produce high-density jet fuel have concentrated on increasing the naphthene content of the fuel. These approaches generally involve tapping different hydrocarbon streams or sources than are presently used for jet fuel, and altering the molecule type by chemical reaction.

The USSR already uses a high density fuel in some applications as was proven by analysis of the fuel from a defected Mig (1976, Project Stablemate). This fuel proved to be primarily composed of hydrotreated light cycle oil (LCO) from the catalytic cracking (FCC) process. Subsequent investigations funded by the U. S. Air Force concentrated on producing a similar fuel from the hydrotreating of steam cracker light pyrolysis oil<sup>(2)</sup> as well as hydrotreating LCO<sup>(3)(4)(5)</sup>. Numerous studies have also been conducted on the conversion of synfuels<sup>(6)(7)(8)(9)</sup> (coal tar, tar sands extract, shale oil) to jet fuels, although not necessarily high density fuels. All the above work has confirmed that high density fuel can be readily produced but not necessarily for the same cost as conventional jet fuel.

J & A Associates, formerly the Tosco Corporation Research Center, became aware of these studies in early 1985. From extensive experience with refinery streams and naphthenic crude oils, J & A personnel judged the present production of certain refinery streams could satisfy an immediate high-density fuel need and some adjustments in refinery operations could satisfy conceivable future needs for high-density fuels. Therefore, J & A Associates submitted a proposal to specifically evaluate two sources of high density jet fuel:

A. Straight-run cuts from naphthenic crude oils.

B. Refinery hydrocracker product streams

These two sources were to be examined as to availability, quality of the product, and the need for further processing (upgrading). Results of that study, performed during August, 1985 through January, 1986, are reported here.

Section III  
Scope of Work

The scope of this work was to evaluate the present and potential availability and quality of JP-8X (present high density JP-8) and JP-11 (future high density fuel) from these two sources:

- A. Naphthenic crude oils in the continental U.S.
- B. U. S. Refinery hydrocracker streams

Other sources of high density jet fuel, such as synfuels, and processes not yet in use, were excluded from this study. This study also excluded foreign crude oil and foreign refineries. Analyses performed were limited to those listed in the "Statement of Work, Subcontract G-9046(8827)-544" (Attached as Appendix B).

Primary tasks of this work were:

- A. Identification of U. S. naphthenic crudes, their rate of production and the reserves remaining.
- B. Analysis of JP-8X and JP-11 cuts from representative crudes, comparison with tentative specs, and performing limited upgrading test.
- C. Survey of U. S. hydrocrackers and procurement of JP-8X and JP-11 candidates.
- D. Analysis of samples, comparison with tentative specs, and re-distillation if necessary.
- E. Estimation of present and potential production of high density jet fuel from both sources.

## Section IV

### Naphthenic Crude Oils as a Source of High Density Jet Fuel

Present jet fuels consist primarily of straight-run (virgin) fractions from conventional crudes. These conventional crudes are predominately paraffinic and result in jet fuels that are approximately 50% paraffins in composition. Crude oils that contain high proportions of naphthenes (cyclic paraffins) will result in jet fuels high in naphthenes and thus, greater in density than conventional fuels.

#### A. Work Performed

In order to identify naphthenic crudes, determine availability now and in the future, and assess the quality of the resulting jet fuel, these tasks were undertaken:

1. A crude oil survey was conducted using the NIPER (Bartlesville Energy Technology Center) crude oil data base which contained over 9000 U.S. crude assays. Naphthenic crudes were identified by (a) crude oil classification labels (b) the Bureau of Mines Correlation Index (c) densities of fractions in the kerosene range, and (d) PNA analyses, where available.
2. Geographic locations of the crudes identified above were plotted, and individual oils were condensed into fields or geographic areas. These fields were then matched against established fields for which production and reserve data were known.
3. Certain fields were targeted either because of size or geographic diversity. Then, pipelines or wells within these fields were targeted in order to obtain representative samples.
4. Crude oil samples were obtained and fractionated by True Boiling Point apparatus (TBP, or 15/5 distillation) to the desired high density jet fuel boiling ranges.
5. The jet cuts were then analyzed, and compared with tentative high density fuel specifications.
6. Several samples that failed to meet specs were re-distilled, blended, or upgraded (clay treatment, hydrotreating).

#### B. Results

The work described above proved that high density jet fuel can be made from the straight-run fractions of naphthenic crudes. It also generated the estimate below on the potential availability of one high density fuel under consideration, JP-8X.

Table 1  
TENTATIVE SPECIFICATIONS FOR HIGH DENSITY JET FUELS

	Conventional		Near Term HD	Future HD
	JP-5	JP-8	JP-8X	JP-11
*API Gravity	36-48	37-51	< 37	< 25.7
Specific Gravity, g/cc	0.788-0.845	0.775-0.840	> 0.840	> 0.900
Smoke Pt, mm	> 19	> 25.0(1)	> 15.0	--
Freeze Point, °F	< -51	< -58	< -51	< -51
Vis at -4 °F, cs		8.0	--	--
Vis at -40 °F, cs	< 16.5 at -30	--	< 20	< 40
Aromatics, vol %	< 25	< 25	--	--
D-86 Boil Range, °F	550 EP	572 EP	360-570	360-700
Flash Point, °F	> 140	> 100	> 140	--
Sulfur, wt %	< 0.4	< 0.4	< 0.4	--
JFTOT (Thermal Stability)	--	--	Pass 260°C	Pass 260°C
Pressure drop, mm Hg	< 25	< 25		
Tube Deposit Number	< 3	< 3		

(1) 20 mm and less than 3% naphthalenes is an alternate spec.

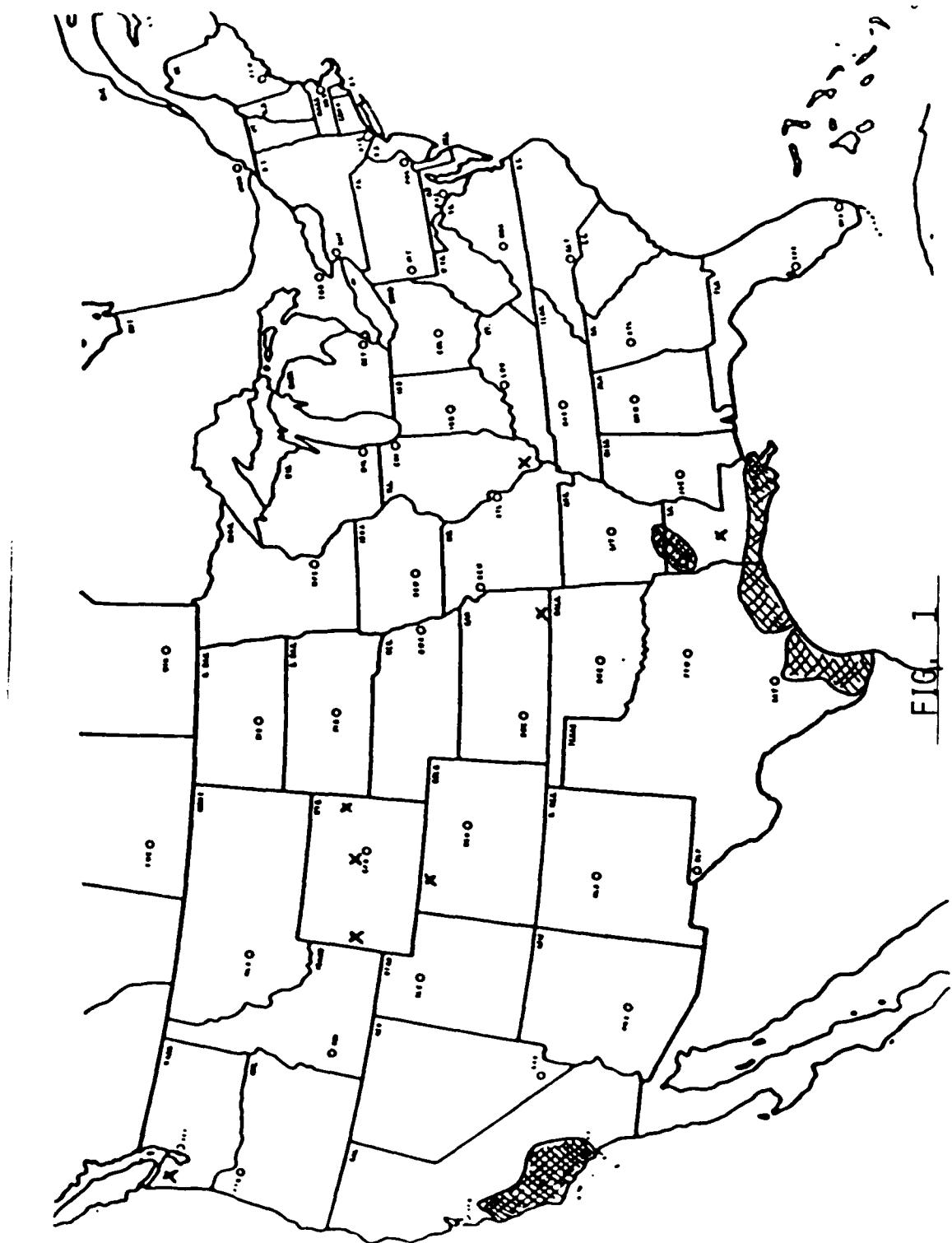
Table 2  
NAPHTHENIC CRUDE LOCATIONS\*

<u>State</u>	<u># of Crudes</u>	<u>Counties</u>
Arkansas	3	Quachita, Union, Nevada
California	71	Kern, Los Angeles, Santa Barbara, Monterey, Fresno, San Louis Obispo, Ventura, Santa Clara, off shore.
Colorado	1	Routt
Illinois	1	Union
Louisiana	40	Iberia, Caddo, Vermillion, Calcasieu, Acadia, St. Martin, Iberville, Terrebonne, Ascension, Cameron, La Salle, La Fourche, Plaquemines, Bossier, off shore (Main Pass, South Pass)
Kansas	3	Labette, Allen, Neosho, Montgomery
Texas	241	Harris, Jefferson, Refugio, Victoria, Galveston, Duval, Jackson, Brazoria, Wharton, Orange, San Patricio, Nueces, Van Zandt, Polk, Hardin, Mc Mullen, Jim Hogg, Goliad, Pecos, Atascosa, Hidalgo, Liberty, Fort Bend, Zapata, Webb, Matagorda, Chambers, Kleberg, Washington, Austin, Starr, Bee, Live Oak
Washington	1	Jefferson
Wyoming	3	Natrona, Sublette, Weston
	364	

\* Results from a search of the over 9000 assays in the NIPER (Bartlesville Energy Technology Center) crude oil data bank.

U.S. NAPHTHENIC CRUDES

FIG. 1



## ESTIMATE OF JP-8X AVAILABLE FROM NAPHTHENIC CRUDES

<u>State</u>	<u>Naphthenic Crude Annual Production</u>	<u>% SR Jet Fuel</u>	<u>Potential JP-8X</u>
Calif.	311.1 MM Bbl	15	46.7 MM bbl/year
Texas	41.2 MM Bbl	35	14.4 MM Bbl/year
Louis. Ark.	14.6 MM Bbl	25	3.7 MM Bbl/year
	<b>TOTALS 366.9 MM BBL</b>		<b>64.8 = 0.18 MM Bbl/day</b>
			<b>= 0.36 MM Bbl/day*</b>
			Blended with conventional streams

JP-8X is a near-term high density fuel having essentially all the properties of conventional JP-8 except for greater density and a lower smoke point. A second high density fuel under consideration is JP-11, a second generation or future fuel. The specifications on JP-11 are much more difficult to meet and straight-run fractions from naphthenic crudes could not qualify as JP-11. The difficulty of meeting JP-11 specs will be examined as specific crudes are discussed. The tentative specifications for JP-8X and JP-11 are given in Table 1.

### C. Discussion

The NIPER crude oil data bank search and in-house crude assay data resulted in identifying 502 naphthenic crudes, less than 6% of the assays examined. Of these, only 364 crudes contained enough material in the kerosene boiling range to be considered. The locations of these crudes are given in Table 2 and Figure 1. From Figure 1 it is seen that naphthenic crudes are found primarily in California and along the Gulf Coast and are not found in the large producing areas of Texas and Oklahoma.

Table 3 gives the results of matching those individual crudes to large fields that have production and reserve data. Table 3 also indicates which crude oil samples were requested and obtained. The process of classifying these fields as naphthenic involves some risk, since different oils can be produced from different levels and since assay data may not be representative of the whole formation. However, the NIPER data, obtained before defining the fields, and the data obtained on the samples actually received, were in good agreement, confirming the nature of the targeted fields.

Table 3 shows the largest naphthenic crude oil production by far is in California (85% of naphthenic production), and particularly in the San Joaquin Valley (60% of naphthenic production). Reserves estimated in these fields presently give a 13 year supply, and California reserve estimates have been increasing, due to greater application of enhanced recovery methods<sup>[7]</sup>.

The Gulf coast area also contains significant naphthenic crude resources. These fields have been in production for many years and at present rates of production contain slightly less than 10 years of reserves.

- \* The primary blending stream considered is straight-run from Alaskan North Slope Crude. This material by itself almost meets JP-8X specs. ANS crude is produced at the rate of 600.9 MM Bbl/day and contains 18 vol % JP-8X boiling range material.

Table 3

## U.S. NAPHTHENIC CRUDE RESERVES, JANUARY 1985

<u>State</u>	<u>Field</u>	<u>Annual</u>	<u>Cum Prod, MM Bbl</u>	<u>Estimated</u>
		<u>Production</u> <u>MM BBL</u>		<u>Reserves, MM bbl</u>
Arkansas	Smackover	3.8	543	18*
California	S. Belridge	43.0	430	364*
	Buena Vista	2.0	641	19
	Coalinga	9.7	710	84
	Cymric	5.0	171	38
	Elk Hills	56.2	734	795*
	Fruitvale	1.0	112	12
	Kern Front	2.5	165	25
	Kern River	48.1	1014	983*
	McKittrick	4.6	254	28
	Midway Sunset	47.5	1652	489*
	Total SJV Valley	219.6	5883	2837
	Cat Canyon	5.1	274	65
	San Ardo	8.1	384	154*
	Santa Maria Valley	3.0	190	51
	Beta	15.0	23	~ 400*
	Brea Olinda	2.7	375	68
	Huntington Beach	9.2	1039	89
	Inglewood	3.6	333	64
	Long Beach	3.4	899	31
	Montebello	0.5	190	4
	Torrance	2.5	205	11
	Wilmington	38.4	2149	393
	Total California	311.1	11944	4167
Louisiana	Caddo-Pine Island	4.3	346	20**
	Jennings	0.4	115	2
	Lake Pelto	0.6	115	20
	Vinton	0.6	135	2
	South Pass, Blk 27	2.3	116	85
	Main Pass, Blk 306	2.6	70	82**
	Total Louisiana	10.8	897	211
Texas	Greta	1.3	144	17
	Lake Pasture	2.6	74	24
	Tom O'Connor	19.2	697	123*
	West Ranch	5.0	369	20
	Magnet Withers	2.5	104	10
	Thomson	6.6	457	49*
	Van	4.0	508	46
	Total Texas	41.2	2353	289
Wyoming	LAK	--	--	20*
	TOTAL U.S.	366.9	15737	4705
All US Crudes		3258	--	28,446
Naphthenic Crude, % of Total		11.3%	--	16.5%

\* Samples received and analyzed.

\*\* Samples requested but not received.

Production data from Petroleum Information, Denver.

Reserve data from Oil and Gas Journal; Energy Information Administration.

Another pocket of naphthenic crudes is found in Northern Louisiana and Southern Arkansas. Again, these fields are old and contain about five years of reserves.

Naphthenic crude production (11.3% of total U.S.) and reserves (16.5% of total U.S.) are greater than the crude search suggested. This may be because the NIPER crude data bank is heavy on Oklahoma and Central Texas crudes and deficient in off-shore assays. This lack of data on off-shore crudes, particularly Louisiana, is an uncertain area in this program. Most efforts to obtain off-shore assay data and samples were unsuccessful and thus the extent of naphthenic production and reserves in the Gulf of Mexico is unknown. However, if 20% of those crudes are naphthenic, an additional 20 MM Bbl can be added to the annual production and another 600 MM Bbl to the reserve data in Table 3.

The crude oil samples requested were generally pipeline samples representative of the field. Of course, pipeline oil compositions may vary with time and with sampling point along the line, therefore introducing some uncertainty into this study. Pipelines present a major problem in isolating certain crude oils because all manner of crudes are blended in along the way. Thus, most naphthenic crudes arrive at refineries diluted, having lost their identities and their ability to produce high density jet fuels.

In California's San Joaquin Valley, this is not a problem. The fields are sufficiently large and similar enough that pipeline samples at the refinery are similar to well-head samples. Thus, unless the pipeline crude is mixed with paraffinic crude at the refinery (such as Chinese or Indonesian), production of naphthenic jet fuel could be easily accomplished.

Along the Gulf Coast, it is more difficult to isolate naphthenic crudes. Here, dedicated pipelines, extra tankage, and blocked-in production runs may be needed in order to produce naphthenic jet fuel. Offsetting these difficulties is the overall better quality of the Gulf Coast naphthenic crudes as compared to the California crudes, which would minimize extra processing costs. Figure 2 illustrates the refinery units needed to produce JP-8X from naphthenic crudes.

The specific crude oils evaluated were as follows:

California:	San Joaquin Valley Composite Crude
	Beta Crude
	San Ardo Crude
Texas:	Manvel Crude
	Refugio Crude
Arkansas:	Smackover Crude
Wyoming:	LAK Crude

The SJV composite crude actually represented the three major heavy crudes in the valley, as is shown in Table 4. Results obtained on the composite are believed to pertain equally to South Belridge, Midway Sunset, and Kern River crudes. The other SJV crude considered was Elk Hills. However, Elk Hills samples proved variable in composition (Table 4), and therefore these samples were not evaluated in this study. Although the Elk Hills samples showed high levels of either paraffins or aromatics, they were primarily naphthenic and would produce high density fuels.

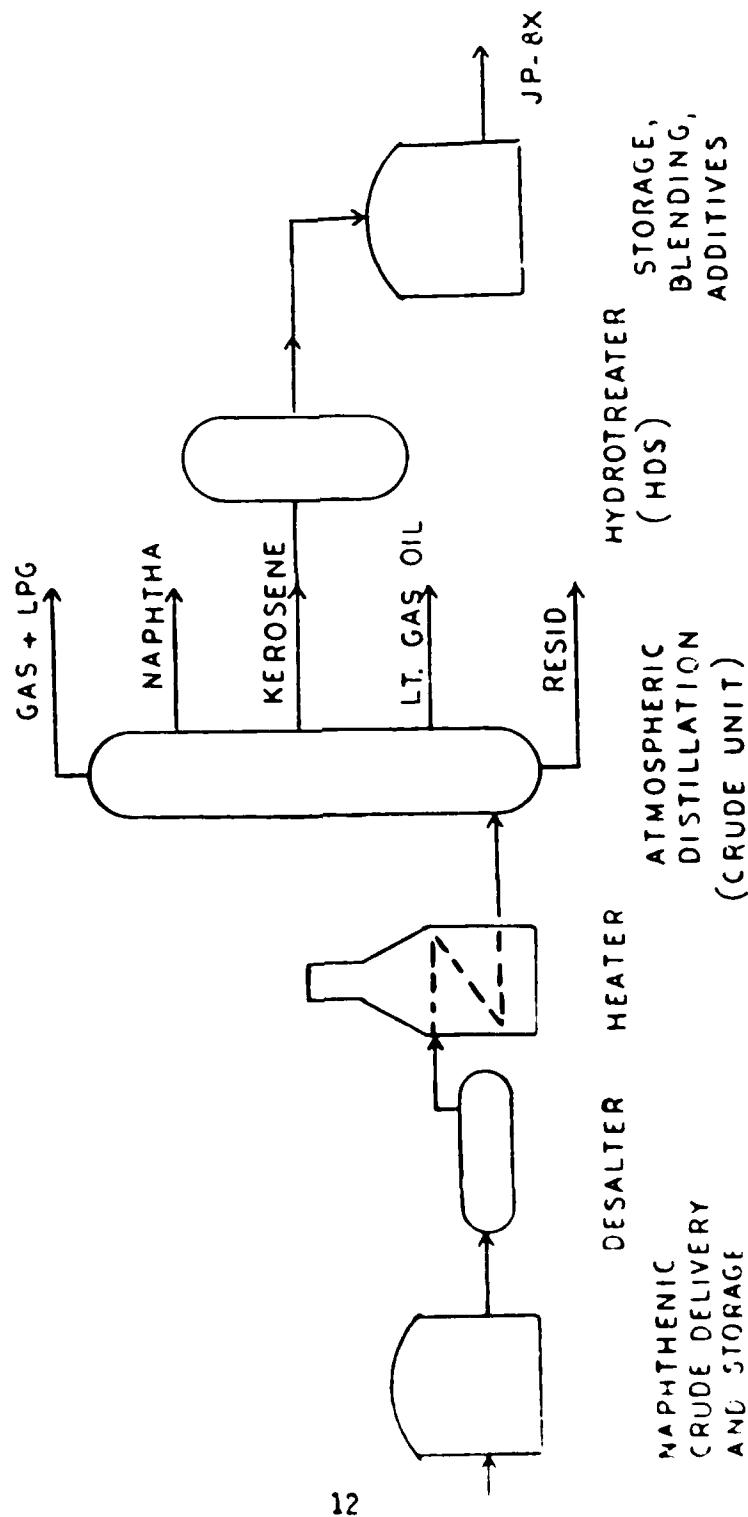


FIG. 2. PRODUCTION FROM NAPHTHENIC CRUDE  
JP-8X

Table 4

## SAN JOAQUIN VALLEY CRUDE COMPARISON \*

	<u>SJV Pipeline Sample</u>	<u>Midway Sunset</u>	<u>Kern River</u>	<u>South Belridge</u>	<u>Elk Hills Shallow</u>	<u>Elk Hills Stevens</u>
Crude °API 60/60	14.1	13.7	13.3	13.7	27.8	35.5
Wt % S	1.06	1.20	1.11	1.02	0.70	0.50
Wt % N	0.66	0.69	0.74	0.75	0.37	0.30
Wt % Con C	7.00	6.76	7.64	6.39	3.76	2.57
IBP 340°F, vol %	1.1	1.2	None	None	22.6	33.3
340-580°F, vol %	14.7	14.3	13.0	15.5	24.2	24.8
°API 60/60	29.5	29.5	28.4	30.5	32.5	37.2
Wt % S	0.36	0.45	0.39	0.34	0.29	0.17
Wt % N	0.02	0.02	0.03	0.02	0.01	0.01
<b>380-480°F Mass Spec Analysis</b>						
Paraffins, wt %	3	1	8	5	8	29
Naphthenes, wt %	82	85	79	74	63	51
Aromatics, wt %	15	14	13	21	29	20
<b>480-520°F</b>						
Smoke Pt, mm	15.2	14.0	15.5	14.2	12	15
Aniline Pt, °F	132	125	132	131	119	138

\* Samples received at the Rocky Flats Research Center.

Conclusion: (1) The SJV pipeline sample is representative of the three major heavy San Joaquin Valley Crudes.

(2) The Elk Hills resource is variable in composition and not as naphthenic as the other major SJV Crudes.

Beta Crude was chosen because it represents a new find (1976) as well as being representative of Los Angeles basin naphthenic crudes. It is an off-shore San Pedro crude very similar to the giant Wilmington field.

San Ardo Crude was examined because it is a large field, geographically removed from the above fields, and it has been the subject of other upgrading studies<sup>(8)</sup>. These three California samples are believed to adequately represent the naphthenic crude resources of California.

In Texas, many smaller fields exist and adequately representing them is difficult. Therefore random crudes from the two largest fields were procured. Manvel Crude, from Brazoria County, south of Houston, represents the Thomson resource, while Refugio Crude (Refugio County, north of Corpus Christi) represented the Tom O'Connor, Greta, and Lake Pasture resources.

For the Northern Louisiana/Southern Arkansas region, Smackover Crude was examined. A Caddo-Pine Island sample (near Shreveport) had also been requested but failed to arrive in time for analysis.

In Wyoming, a crude that was unusually high in naphthenes was discovered. Although this crude (LAK) was barely in production (10 Bbl/day), the size of the resource (50 MM Bbl in place) and the geographic location made this crude worthy of study.

For Southern Louisiana, two crude samples had been requested, one from Main Pass production (off-shore, east of New Orleans) and one from a pipeline outside of New Orleans. Neither of these samples arrived in time for analysis and therefore no results are available for southern and off-shore Louisiana.

Alaskan North Slope Crude was also examined but only as a blending stock since it is an intermediate crude. ANS production and reserves are greater than the total naphthenic crudes given in Table 3 and could thus double the availability of JP-8X.

TBP distillations performed on these crudes in order to obtain the jet fractions, are given in Appendix 1. Analytical results on the JP-8X and JP-11 fractions are given in Tables 5 and 6, respectively. The results for each crude are individually discussed below.

#### San Joaquin Valley Composite Crude

This crude oil is heavy (14°API), containing very few light ends (1% gasoline), and being high in nitrogen (0.6 wt %). Distillation yields about 15 vol % of JP-8 range material, but this jet cut is deficient in light ends. The high nitrogen content also makes the jet cut unstable and hydrotreating is almost certainly required. Sulfur content is marginal, and as distilled, the viscosity at -40°F is too high for JP-8X. The viscosity can readily be adjusted by blending in lighter material or by taking the final cut at a lower temperature. The density and freeze point are much better than specs.

TABLE 5  
Straight-Run JP-8X  
Candidates from Naphthenic Crudes

Crude Name	SJV	H/T SJV	H/T SJV/ANS(2)	Beta	San Ardo	Manvel	Refu- gio	Smack- over	LAK(1) Blend
State of Origin, TBP Traction, °F	Tentative JP-8X Specs	CAL 360-591 14.7	CAL 350-580 15.9	CAL/CAL 325-550 11.5/15.5	CAL 350-565 13.9	CAL 340-580 19.1	TEXAS 350-563 32.2	ARK 340-570 42.6	WYO (1) 18.9/14.2
Analyses									
API Gravity,*	<37.0	29.5	32.1	32.9	29.1	31.4	34.5	35.7	34.8
Specific Gravity	>0.8400	0.8791	0.8650	0.8620	0.8610	0.8809	0.8684	0.8524	0.8511
Freeze Point, °F	<-51	-103	-67	-49	-58	-85	<-67	-45	-94
Vis at -40°F, cS	<20	44.0	49.0	21.5	50.7	33.4	48.1	20.8	-90
Flash point, °F	>140	NA	NA	128	NA	NA	108	147	17.5
JFTOT results							(3)	(3)	132
pass 260 °C							Pass	Pass	
Smoke point, mm	>15	NA	NA	16.2	19.4	NA	18.4	15.3	Pass
Sulfur, wt%	<0.4	0.36	0.002	0.016	2.27	0.74	0.10	0.09	24.8
Hydrogen, wt%	---	NA	NA	12.56	NA	NA	NA	0.39	0.03
D-86 Distillation, °F								NA	13.08
IBP/5 vol% over	360	344/405	355/438	338/397	369/407	275/420	387/415	363/402	295/360
10/20	---	419/437	452/469	416/441	418/429	435/451	424/438	413/433	293/351
30/40	---	459/475	483/494	457/472	442/457	464/476	453/468	451/466	373/400
50/60	---	491/510	506/518	487/498	470/486	492/508	477/488	481/495	421/443
70/80	---	592/552	531/545	509/519	502/517	525/543	501/512	508/521	465/487
90/95	---	572/575	566/581	528/533	539/554	565/577	528/543	541/554	510/538
EP	570	576	585	535	557	580	559	574	564/572
								575	581
Structural analysis, vol%									
Paraffins	NA	NA	NA	NA	NA	15.2	17.8	23.6	NA
Cycloparaffins									
Di-cycloparaffins									
Tri-cycloparaffins									
Alkyl Benzenes									
Benzocycloparaffins									
Benzodicycloparaffins									
2 Ring Aromatics									
Heavier aromatics plus polars									
TOTAL								100.0	100.0

(1) 65 vol% LAK 370-600°F, 35 vol% Wyo Sweet 320-440°F, clay treated.

(2) 60% SJV, 40% ANS.

(3) Could not pass without hydrotreating.

NA = Not Analyzed.  
H/T = Hydrotreated.

16.2%    28.8%  
Aromatics Aromatics  
by FIA by FIA

20.8%  
Aromatics  
by FIA

Light hydrotreating (700 psig, 650°F) of a 60/40 blend of SJV distillate and Alaskan North Slope distillate also yields an excellent JP-8X, as is shown in Table 5. This sample is an actual refinery stream, produced at the rate of 6600 Bbl/day. Presently this stream is part of the #2 fuel oil (diesel) production and is not sold as kerosene or jet fuel. Other California refineries that process primarily SJV crude are expected to have similar streams.

Thus, SJV crude definitely has potential as a source for JP-8X. However JP-11 cuts (360-700°F) from SJV crude are unable to meet both density and low temperature viscosity specs (Table 6). Hydrotreating will again be required which will make the cuts less dense (higher in API gravity) but have little effect on low temperature properties. Severe hydrotreating of SJV diesel in fact produced a JP-11 cut that met neither the gravity spec nor the low temperature viscosity spec (Table 7).

#### Beta Crude

Beta Crude is also a heavy crude (16°API), high in sulfur (3.4%) and nitrogen (0.7%) but containing substantial light material (about 10%). Upon distillation it yields about 14% jet fuel. As is the case with SJV distillate, this cut is unstable and requires hydrotreating. The sulfur content is also high (2.3%) but this may be partially from contamination from Hondo Crude, which is very high in sulfur. (Beta and Hondo were stored in the same tankage at the Beta sampling point). Although the Beta jet cut is not as dense as the SJV cut and the low temperature properties are not as good, the jet cut should meet the tentative JP-8X specs after hydrotreating.

Beta is also not expected to make acceptable JP-11. Since both San Ardo and SJV appeared to be better JP-11 sources than Beta and since both failed, a Beta JP-11 cut was neither taken nor analyzed. Hydrotreating tests were also not performed on Beta fractions.

#### San Ardo Crude

San Ardo Crude is the heaviest (13°API) and highest nitrogen content (0.9%) crude of the California crudes examined. It contains 2% sulfur and has about 2% light material (-350°F). However, it yields a greater volume (19%) and greater density jet cut (29.1°API) than the crudes examined above. As with the above crudes, hydrotreating will be required to remove nitrogen and sulfur and produce a thermally and oxidatively stable fuel. Unfortunately, no pilot plant tests were completed on San Ardo distillate. Hydrotreating results are expected to be similar to those obtained on SJV distillate, however, except in that hydrogen consumption will be higher.

Again, San Ardo is not expected to make JP-11 specs. A 250-650°F fraction exhibits the desired low temperature properties (Table 6) but the API gravity is 3° too high and is expected to be several degrees higher after hydrotreating.

TABLE 6  
Potential JP-11 Candidates  
from Naphthenic Crudes

Not Analyzed  
None Detected  
Hydrogenated  
H/T

### Manvel Crude

Manvel Crude from Texas is a sweet (0.2% sulfur), low nitrogen (0.02%), medium gravity crude (27°API). Upon distillation, it yields 32% of 31.4°API jet fuel. However, the low temperature viscosity on this cut is a little high and the cut point should be lowered about 30°F to make specs. As distilled, the smoke point was 18.4 mm, better than most other JP-8X candidates. This straight-run product has no stability problems and appears to make an exceptional JP-8X. This material is currently being produced at the Texaco Port Arthur refinery at the rate of 1600 Bbl/day and is blended with more paraffinic streams and sold as avjet. (The Port Arthur refinery trucks in naphthenic crudes for use in naphthenic lube oil production).

The JP-11 cut almost meets the low temperature specifications but is 5° higher than desired in API gravity. Again, it appears impossible to satisfy both density and low temperature requirements. Relaxation of the density spec to 30°API might qualify Manvel Crude as a source of JP-11.

### Refugio Crude

Refugio Crude, also from Texas, is a relatively light crude (33°API), low in sulfur (0.2%) and nitrogen (0.03%). Upon distillation, it yields almost 43% of jet fuel range material. This cut passes all JP-8X specs except it is 6°F high on freeze point. Distilling to a lower end point should lower this freeze point and may improve the marginal smoke point (15.3 mm). Refugio JP-8X should not need extra upgrading except perhaps a clay treatment.

Due to a high paraffin content (24% in the JP-8X fraction) the Refugio JP-11 cut cannot make the low temperature specs (Table 6). The API gravity is also much higher than desired, and adjustment of the JP-11 density spec will not help Refugio crude qualify.

### Smackover Crude

Smackover Crude from Arkansas is a medium gravity (24°API) medium sulfur (2%), moderate nitrogen content (0.05%) crude. It is not as highly naphthenic as the other crudes examined and is classified as "Intermediate" (between paraffinic and naphthenic). Upon distillation, it yields almost 24% JP-8 range material that meets all the JP-8X specs except for smoke point (14.4 mm) and stability. The stability problems are due to high sulfur (0.4%) and nitrogen content (0.01%) and should be eliminated by light hydrotreating. It is not known whether this will also improve the smoke point, since no hydrotreating tests were performed on Smackover distillate.

As with Refugio Crude, Smackover JP-11 cannot pass low temperature specs due to a high paraffin content. It also appears that relaxation of the density spec will not help Smackover JP-11.

Table 7  
HYDROTREATING OF SAN JOAQUIN VALLEY DISTILLATE

Hydrotreating Conditions

Catalyst used	Union HC-Fa
Reactor temperature, °F	720
Reactor pressure, psig	1450
Hydrogen input rate, SCF/bbl	3419
Liquid hourly space velocity	1.008

Hydrotreating Results

Hydrogen consumption, SCF/bbl	491
Sulfur reduction, %	99.69
Nitrogen reduction, %	99.94
Mass balance closure, wt %	99.82
Vol % recovered as oil	102.37

Analytical Results

	Whole Feed	Whole Product Oil	JP-8X Cut	JP-11 Cut
Vol % of crude	19.4	19.9	15.9	18.4
Vol % of whole product	--	100.0	80.0(1)	92.7(2)
API Gravity	26.9	32.7	32.1	31.7
Specific Gravity	0.8933	0.8618	0.8650	0.8670
Wt % Carbon	86.88	86.78	NA	NA
Wt % Hydrogen	12.53	13.22	NA	NA
Wt % Sulfur	0.54	17 wppm	NA	NA
Wppm Nitrogen	518	0.3	NA	NA
Freeze Point, °F	NA	NA	-67	-69
Vis at -40°F, cs	NA	NA	49.0	62.3
Smoke Point, mm	NA	NA	16.2	NA
D-86 Distillation, °F				
IBP/5% distilled	452/476	151/213	355/438	NA
10/20	485/498	399/457	452/469	
30/40	513/526	482/497	483/494	
50/60	540/553	511/525	506/518	
70/80	567/581	538/558	531/545	
90/95	599/617	579/585	566/581	
EP	619	589	585	
JF TOT	NA	NA	Submitted for testing	NA

(1) 7.3 vol % topped, 12.7 vol % bottoms rejected.

(2) 7.3 vol % topped, no bottoms rejected.

NA Not analyzed.

### LAK Crude

LAK Crude from Weston County, Wyoming is a heavy crude (19°API), lacking in light material, low in sulfur (0.4%) and relatively high in nitrogen (0.2%). It is an undeveloped field containing approximately 50 MM Bbls and is of interest because of its highly naphthenic character and its geographic location. During the initial crude oil survey, a number of crudes similar to LAK turned up in various parts of the country, but most of them were dismissed because:

- (1) They contained insufficient light material to make full-range jet fuel.
- (2) They were isolated crudes that could not be matched to large producing areas
- (3) It was assumed these crudes would lose their identities in pipeline blends and could not be economically isolated for processing.

LAK crude proves that even in the more remote areas of the U.S. it may be possible to produce high density jet fuels.

Upon distillation, LAK crude yields about 17% material in the JP-8 distillation range. However, this fraction is deficient in light material and may not have enough volatility for present jet engines. By taking a little deeper cut (19% overhead) and adding heavy naphtha (320-440°F) from a nearby paraffinic crude (40°API Wyoming Sweet) an excellent JP-8X can be created. Table 5 shows that this blend meets all the specs easily, except it is 8°F low in flash point, which can be easily altered by adjusting the Wyoming Sweet cut points. The most remarkable result is the high smoke point of 24.8 mm, which is 5.3 mm greater than the next best result obtained in this study.

Due to the LAK nitrogen content, a slight discoloration of the jet cut occurred over a period of time. Therefore, the LAK/Wyoming Sweet blend was clay treated (activated attapulgus clay) before submitting it to the analyses in Table 5. It is not known how well this blend would fare without the clay treatment.

As with all the other crudes examined, it appears impossible for LAK or LAK blends to meet both the JP-11 density spec and the JP-11 low temperature specs (Table 8). Heavy LAK TBP cuts are sufficiently dense but too viscous. A blend with Wyoming Sweet is both too viscous and insufficiently dense.

TABLE 8  
LAK Fractions as JP-11

State of Origin TBP Fraction, °F Vol % of Crude	Tentative JP-11 Spec	LAK	LAK	LAK	LAK Blend	LAK
<b>Analyses</b>						
API Gravity	< 25.7	28.7	25.8	24.9	28.6	28.1
Specific Gravity	> 0.9000	0.8833	0.8998	0.9046	0.8388	0.8864
Freeze Point, °F	<-51	-90	-67	NA	<-45	-90
Vis at -40°F, cS	<40	86.8	NA	1481	190.9	135.9
Flash Point, °F	>140	>190	>198	>198	NA	NA
Smoke Point, mm	--	NA	12.3	NA	NA	NA
Sulfur, wt %	--	0.10	NA	0.20	0.17	NA
Hydrogen, wt %	--	NA	NA	NA	NA	NA
LHN, Btu/gal	--	NA	136,209	NA	NA	NA
D-86 Distillation, °F						
1BP/5 vol % over	360	294/430	464/487	478/502	334/374	450
10/20	--	447/465	506/533	520/544	399/464	
30/40	--	478/493	555/570	570/590	518/554	
50/60	--	506/523	588/605	612/632	576/612	
70/80	--	538/556	621/639	647/667	637/660	
90/95	--	583/597	658/671	689/--	691/700	
EP	700	599	671	698	700	520
<b>Structural Analysis, vol %</b>						
Paraffins	NA	NA	12.1	NA	ND	13.2
Cycloparaffins			14.5		65.6	21.2
Di-cycloparaffins			32.4		ND	ND
Tri-cycloparaffins			10.4		ND	ND
Alky1 Benzenes			7.8		ND	ND
Benzocycloparaffins			5.7		ND	ND
Benzodicycloparaffins			5.0		ND	ND
2 Ring Aromatics			10.1		ND	ND
Heavier Aromatics + Polars			2.0		ND	ND
<b>TOTALS</b>					<b>100.0</b>	

(1) 82 wt % LAK 360-740°F, 18 wt % Wyoming Sweet 320-440°F.

NA Not Analyzed  
ND Not Detected.

Because LAK crude is one of the most naphthenic crudes examined, some additional attempts were made to produce JP-11. A lower temperature cut (600°F) still did not reduce viscosity enough and sacrificed density. A very narrow cut (480-520°F) was also analyzed and had the same shortcomings. Perhaps different LAK blends using heavy reformate or heavy cat cracker naphtha (both high in aromatics and isoparaffins) could approach the JP-11 specs. However, the scope of the program allowed only limited testing and these blends were not examined.

Therefore, it appears the present JP-11 specs are unattainable using straight-run fractions from naphthenic crudes. A relaxation of the density spec to 30°API may allow some crudes or blends to qualify.

#### Alaskan North Slope Crude

This crude was not analyzed as a JP-8X or JP-11 source because, compared to other crudes, it was relatively low in naphthenes. However, a crude assay is included in the appendix because:

1. ANS may produce a marginal straight-run JP-8X
2. ANS blended with California crudes will definitely produce an acceptable JP-8X,
3. The ANS production rate and reserves are huge compared with the other more naphthenic crude oils, and could double the availability of JP-8X.

J & A's most recent data (1982) indicates the JP-8 straight-run fraction will have the following properties:

37-38°API	Structural composition:
0.2% sulfur	30% paraffins
18 mm smoke point	45% naphthenes
-40°F freeze point	25% aromatics

This cut will probably require hydrotreating, which will increase API gravity several degrees, and may be fractionated lower to decrease the freeze point, again increasing API gravity. However, blended with hydrotreated SJV distillate, a very good JP-8X candidate results, as is shown in Table 5. This stream presently exists in at least one, and probably in about ten California refineries, which process primarily ANS and SJV crudes.

As with the other crude oils, ANS is not expected to produce an acceptable JP-11.

## Section V

### High Density Jet Fuels from Refinery Hydrocracker Streams

Besides occurring naturally in certain crude oils, naphthenes (cyclic paraffins) can also be manufactured by chemical processes. One of the simplest and most direct methods involves the saturation or addition of hydrogen to aromatic compounds. This process involves high hydrogen partial pressure (over 1000 psi) and moderately high temperature (around 700°F) as well as a hydrogenation catalyst.

This reaction is carried out every day in numerous refineries that utilize hydrocrackers. The primary feed for these hydrocrackers consists of cat cracker light cycle oil, which is the cat cracker (FCC) product oil boiling between 430-650°F. The lighter product oil is used as gasoline blending stock while the heavier product oil is recycled to the FCC, sold as fuel oil, or used as feedstock for needle coke manufacture. The light cycle oil (LCO) is a highly aromatic material that cannot meet diesel gravity and cetane specs and is therefore considered to be an undesirable, low value stream. Due to the nature of the cat cracking process, LCO is always high in aromatics, regardless of FCC feedstock composition. LCO comprises around 20% of the FCC liquid product and is generated in the U.S. at the rate of over 1 MM Bbl/day.

Hydrocracking can convert this low value stream to higher value gasoline, kerosene, and diesel fuel. Hydrocracking is generally a two-stage process, the first stage consisting of severe hydrotreating (2000 psig, 750°F) in order to remove all traces of sulfur, oxygen, and nitrogen. The 2nd stage is the actual hydrocracking process where molecules are saturated, carbon rings are opened, and carbon chains are broken. This 2nd stage is less severe but generally requires a noble metal catalyst which is easily poisoned, explaining the need for the 1st stage. By adjusting feeds, severities (temperature, pressure, space velocity), catalyst type, and recycle rates, the hydrocracker can be made to produce essentially all gasoline, all diesel, or a mixed slate in between.

The diesel and kerosene product streams, having originated from a highly aromatic feedstock, are high in naphthene content, and proportionately more dense than similar boiling range conventional streams. They therefore could serve as a source of high density jet fuel.

#### A. Tasks Performed

In order to determine the present and potential capability to produce high density jet fuels and in order to assess the quality of those fuels, the following tasks were performed:

1. A refinery survey was conducted to identify hydrocracker sites and capacities.
2. Hydrocracker operators were contacted and samples of kerosene - diesel product streams were requested.
3. Samples were analyzed, compared with tentative high density specs, and redistilled if necessary.
4. For samples that met most of the specs, stream size data were obtained and used to generate an estimate of overall availability.
5. Modifications of the hydrocracking process that could maximize high density jet fuel production were examined.

#### B. Results

An estimate of present and potential JP-8X production, based on the above work showed that all military needs and most civilian needs could be fulfilled by hydrocracker production.

#### High Density Jet Fuel (JP-8X) from U. S. Hydrocrackers

<u>Operating U. S. Hydrocrackers</u>	<u>Total Capacity Bbl/day</u>	<u>Estimated Present H/C Production of Kerosene and Diesel, Bbl/day</u>	<u>Estimated High Density Jet Production</u>	
			<u>Present, Bbl/day</u>	<u>Potential Bbl/day</u>
37	1.07 MM	0.32 MM	0.17 MM	0.85 MM

1985 Total U.S. consumption of kerosene type jet fuel      approx. 1.0 MM  
1985            U.S. Armed forces consumption only      approx. 0.3 MM

The present production data are based on results from samples and stream data obtained from 10 operating hydrocrackers (27% of the total). The potential production estimate assumes that essentially all hydrocracking operations maximize the production of jet fuel.

Maximizing high density jet fuel production may involve some need for refinery modifications, such as:

1. Replacing hydrocracker catalyst
2. Revamping or replacing present fractionators
3. Building extra storage (tankage)
4. Restricting hydrocracker feed to aromatics stocks.

Maximizing high density jet fuel production also means that the economic incentives would have to be greater than for producing gasoline from the same feedstocks. Both fuels are sold by volume, but because gasoline is composed of smaller molecules, about 20 vol. % more gasoline than jet fuel can be produced from the same feed. Another consideration is that over 10% of total U.S. gasoline production would be eliminated by maximizing jet fuel production.

As was the case with naphthenic crude oils, no successful JP-11 candidates were found. Even with the relaxation of JP-11 specs, it is doubtful that hydrocrackers can produce this long term high density fuel.

#### Discussion

A refinery survey resulted in identifying 37 U.S. operating hydrocrackers, as listed in Table 9 and illustrated in Figure 3. Their combined feed throughput is 1.07 MM Bbls/day. Since the process adds hydrogen rather than rejecting carbon (e.g., FCC, coking) the average volumetric yields are greater than 120% of input. As discussed above, hydrocrackers are very versatile units and gasoline/jet/diesel production rates tend to swing during the year, depending upon inventories and economics. This makes it difficult to obtain accurate production rates. Also, as catalysts age, are regenerated, or are replaced, yields and compositions of products are significantly altered.

Table 9 also indicates which refineries supplied samples for analysis. All areas of the U.S. were well represented, except for the greater Los Angeles area which contains seven hydrocrackers. However, hydrocracker streams from these refineries are expected to be similar to those from the San Francisco area.

Table 10 gives screening analyses performed on the samples received. (Several refineries sent two samples each). From the API gravity and the D-86 distillation data, the samples were either rejected, analyzed as received, or re-distilled to meet flash point or end point specs. The samples that were further analyzed (3 of them re-distilled) are given in Table 11 and 12. Individual samples are discussed below.

FIG. 3

U.S. HYDROCRACKER DISTRIBUTION

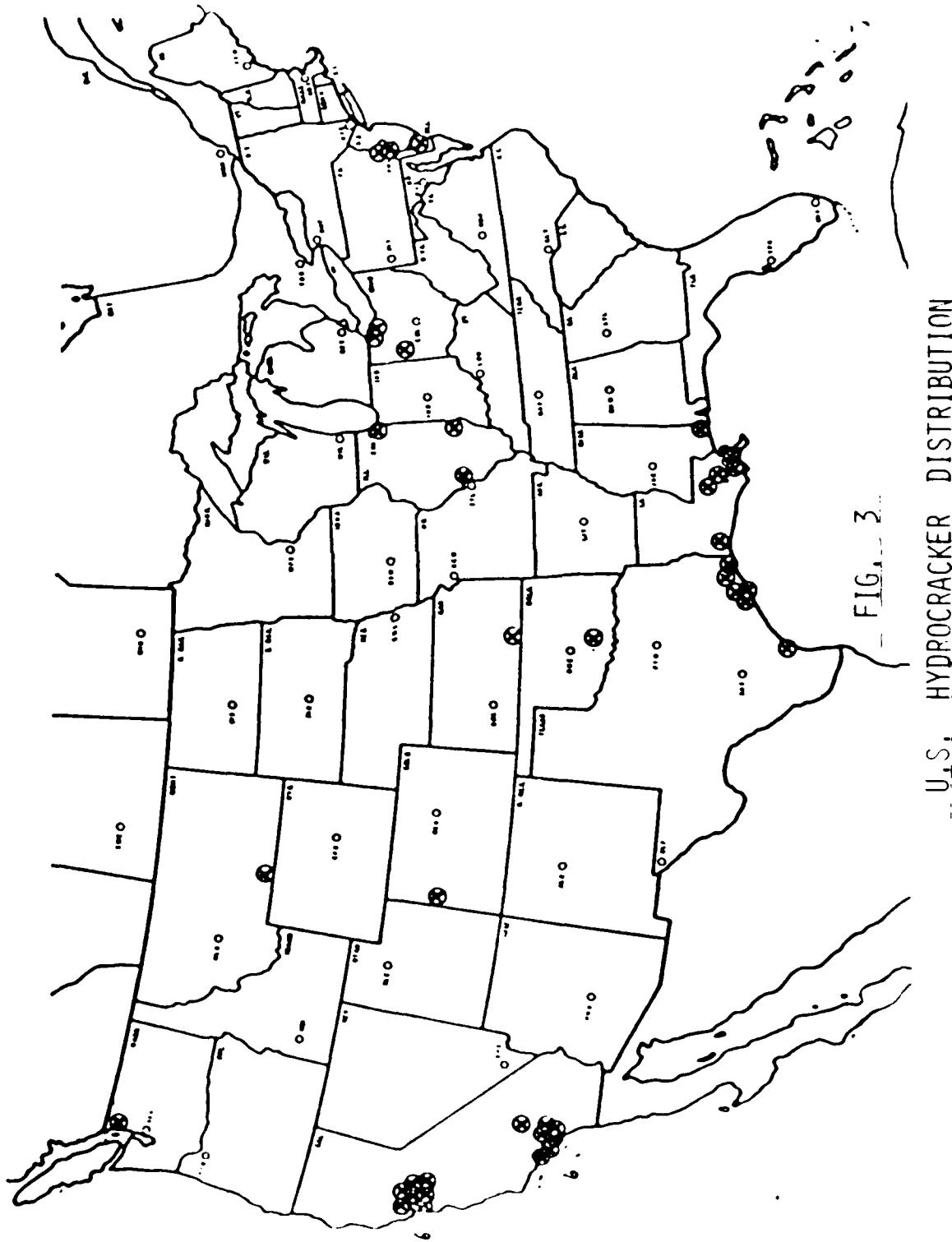


FIG. 3

U.S. HYDROCRACKER DISTRIBUTION

Table 9  
U. S. HYDROCRACKERS(1)

<u>State</u>	<u>Company</u>	<u>Location</u>	<u>Capacity, Bbl/da.</u>
Alaska	Texaco	Kenai	7,500
California	Arco	Carson (LA)	21,000
	Chevron	El Segundo (LA)	43,000
	Chevron	Richmond (SF)	107,500
	Exxon	Benicia (SF)	28,000
	Golden West	Sante Fe Springs (LA)	11,000
	Mobil	Torrance (LA)	21,700
	Pacific Refining	Hercules (SF)	3,000
	Shell	Martinez, (SF)	20,000**
	Texaco	Wilmington (LA)	20,000
	Tosco	Bakersfield	5,000*
	Tosco	Martinez (SF)	20,000**
	Union	Los Angeles	21,000
	Union	Rodeo (SF)	30,000
Colorado	Gary	Fruita (Western Colo.)	5,000*
Delaware	Texaco	Delaware City	19,000**
Hawaii	Hawaii Independent	Ewa Beach	12,000**
Illinois	Clark	Blue Island (Chic)	11,000
	Marathon	Robinson (SE Illinois)	22,000**
	Shell	Wood River (St Louis)	33,500
Kansas	Total	Arkansas City (S Centr. Kansas)	3,200**
Louisiana	Citgo	Lake Charles	30,000**
	Exxon	Baton Rouge	24,000
	Shell	Norco (New Orleans)	27,700
	Tenneco	Chalmette (New Orleans)	20,000*
	Texaco	Convent (New Orleans)	35,000
Mississippi	Chevron	Pascagoula	68,000
Montana	Exxon	Billings	4,900
Ohio	Standard	Lima (W Centr Ohio)	20,000
	Standard	Toledo	35,000**
	Sun	Toledo	26,000
Oklahoma	Kerr Mc Gee	Wynnewood (South Central Okl)	5,000
Pennsylvania	Arco	Philadelphia	30,000
	B.P.	Marcus Hook (Philadelphia)	25,000
Texas	Amoco	Texas City (Houston)	113,000
	Coastal States	Corpus Christi	10,000*
	Exxon	Baytown (Houston)	19,000
	Mobil	Beaumont (Extreme SE Texas)	32,000
	Shell	Deer Park (Houston)	15,000
	Texaco	Port Arthur (Extreme SE Texas)	15,000**
Washington	Arco	Ferndale (North of Seattle)	49,000**
TOTAL US H/C Capacity			1,068,000
Dedicated to distillate upgrading (LCO, etc.)			821,500
Resid upgrading, dewaxing, etc.			246,500

\* = Shut down or on turn-around.

\*\* = Submitted H/C kerosene samples

(1) Data from Oil and Gas Journal, 1985.

Table 10  
"AS RECEIVED" HYDROCRACKER SAMPLES

<u>Refinery</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>J</u>
API Gravity,	39.2	40.8	40.4	49.8	41.0	33.5	37.2	43.4	39.1	49.0
Specific Gravity	0.8291	0.8213	0.8234	0.7804	0.8205	0.8576	0.8388	0.8090	0.8296	0.7841
D-86 Distillation										34.6
IBP°F	148	338	395	246	313	266	369	189	260	236
10% Distilled	344	448	452	250	386	363	381	366	361	382
30	396	512	481	261	404	437	392	400	387	404
50	428	603	511	289	418	467	405	422	413	346
70	460	658	590	302	440	503	424	439	447	475
90	520	708	703	343	481	554	469	464	494	420
EP	531	711	707	356	501	578	541	470	510	494
										486
										506

### Citgo Hydrocracker Kerosene

This sample from the Lake Charles, Louisiana refinery was topped 12% in order to approach the target boiling range and flash point. The topping was performed on a D-1160 apparatus rather than a TBP column, resulting in a rather poor cut. Thus, the flash point still could not meet specs (117°F versus 140°F). As shown in Table 11, the density and freeze point also did not meet specs. However, this stream is close to specifications and has potential as either an interim fuel or as blending stock with straight-run naphthenic streams. Perhaps by limiting hydrocracker feedstock to only aromatic materials, such as LCO, this stream could meet the JP-8X specs.

Currently, this stream, before topping, averages 10,500 Bbls/day (after topping, about 9000 Bbls/day would be available as JP-8X). Since this kerosene cannot meet present jet fuel smoke point specs (19-25 mm), it is blended with paraffinic straight-run streams. Therefore, pulling this stream as JP-8X would only impact on the production rate of conventional kerosene jet fuels (Jet A, A-1, JP-5, JP-8).

The Citgo hydrocracker (30,000 Bbl/day capacity) makes primarily gasoline. The kerosene stream (approximately 30% of the product) is the heavier part from once-through conversion and could be recycled to produce more gasoline if gasoline economics were more favorable. Therefore some economic advantages must always exist for JP-8X production in order to guarantee supplies.

As with most hydrocracking operations that are aimed at gasoline production, a heavier product stream, that could be evaluated as JP-11, does not exist. Use of less severe conditions or heavier feedstock would result in a heavier product stream.

### Texaco Hydrocracker Kerosene

This sample, from the Port Arthur, Texas refinery is very similar to the Citgo sample above. It also required topping (15%) and came close to meeting flash point specs (135°F versus 140°F). This sample also failed the density and freeze point specs, but again, by adjusting the hydrocracker feed or by blending off this stream it could be used as JP-8X. The smoke point on the topped sample, however, was marginal, at 15.0 MM.

This stream, produced at 4000 Bbl/day (3400 after topping) is again the heavy part of once-through conversion, and is subject to other uses. It is presently blended into "avjet" along with straight-run materials.

The Port Arthur refinery processes a number of naphthenic crudes (Manvel, Pickett Ridge) and segregates these crudes for use in lube oil manufacture. This means straight-run naphthenic blending stocks for JP-8X are readily available, and the hydrocracker kerosene need not meet, but only approach, the JP-8X specs.

Table 11

## HYDROCRACKER STREAMS AS JP-8X

Refinery	Location (State)	Tentative JP-8X Specs	Citgo Product Topped 9000	Texaco Texas Product Topped 12# 3400	Texaco Delaware #2 Fuel Oil 85% OH 15,000	Tosco Cal Recycle	Tosco Cal Intermediate	Shell Cal Intermediate
Analyses								
API Gravity	<37.0	38.6	38.7	30.3	37.2	33.5	34.6	
Specific Gravity	>0.8400	.8321	0.8313	0.8745	0.8388	0.8576	0.8518	
Freeze, Pt, °F	<-51	-32	-29	-45	-46	-55	-55	
VIS at -40°F, CS	<20	9.9	7.9	18.6	10.2	14.5	7.7	
Flash Point, °F	>140	117	135	124	190	NA	141	
JFTOT Results								
Pass 260°C Pass	--	NA	NA	NA	NA	NA	Pass	
Smoke Point, min	--	16.8	15.0	14.4	16.0	17.5	16.2	
Sulfur, ppm	--	28	<2	24	<2	<2	<2	
Hydrogen, wt %	--	NA	NA	NA	NA	NA	12.14	
D-86 Distillation, °F								
IBP/5 vol % over	360	329/367	339/369	314/378	369/380	266/289	270/368	
10/20	--	383/397	378/387	405/440	381/387	363/414	382/394	
30/40	--	421/427	396/414	445/456	392/398	437/452	404/412	
50/60	--	439/453	431/444	471/487	405/414	467/483	420/428	
70/80	--	471/495	466/488	504/528	424/440	503/529	436/446	
90/95	--	527/550	515/535	557/586	469/497	554/578	460/482	
EP	570	570	554	601	541	578	486	
Structural Analysis, Vol %								
Paraffins	NA	NA	NA	NA	4.7	10.0	15.1	
Cycloparaffins					59.4	28.0	17.0	
Di-cycloparaffins					14.1	25.0	19.6	
Tri-cycloparaffins					ND	ND	3.6	
Alkyl Benzenes					17.9	9.9	23.4	
Benzocycloparaffins					3.9	27.1	13.1	
Benzodicycloparaffins							3.3	
2-Ring Aromatics							4.5	
Heavier Aromatics plus polars							0.4	
TOTALS							100.0	
NA = Not Analyzed								
ND = None Detected								

### Texaco Hydrocracker #2 Fuel Oil

This sample from the Delaware City, Delaware refinery comes from a different hydrocracking operation than for the previous two samples. This hydrocracker processes heavy cycle oil (HCO) and coker gas oil rather than FCC light cycle oil. The result is a relatively heavy product slate, containing about 8% gasoline and 92% diesel. The "as received" #2 fuel oil (diesel) was quite dense (29.7°API) and was therefore evaluated as a JP-11 candidate. A JP-8X cut was made by distilling 85 vol % overhead, and rejecting the bottom 15%.

As is seen in Table 11, the JP-8X cut easily meets the density spec but is 6°F off the freeze point spec. The smoke point is also quite low at 14.4 mm. Rejecting an additional 5% of the bottoms may help both freeze and smoke points and should have little effect on the density. Several percent may also have to be distilled off the front in order to meet the flash point. Thus, about 78% of this stream could be available as JP-8X. In this case, JP-8X production would compete with #2 fuel oil production, rather than gasoline. Since the estimated cetane index of this hydrocracker diesel is only 34 (diesel spec ≥ 40), JP-8X may be the preferred product. This stream is presently produced at 18,000 Bbl/day, or 15,000 Bbl/day of JP-8X after distillation. The Delaware City refinery also makes straight-run Jet A and some of this could be blended into the JP-8X to raise smoke point and lower freeze point.

The entire stream is also a JP-11 candidate. Table 12 compares "as received" analyses with JP-11 specs. As was the case with naphthenic crude oils, it appears impossible to meet both density and low temperature specs. Even by relaxing density specs to 30°API or lower, this material would still have some problems with viscosity and freeze point.

In an attempt to find a JP-11 refinery stream, a mildly hydrotreated (700°F, 750 psi) light cycle oil was obtained from the Lion Oil Refinery at El Dorado, Arkansas. This material, being highly aromatic (62%), was sufficiently dense, but could not meet low temperature specs, showing a freeze point of -2°F (Table 12). However, the sample was higher in paraffins (22%) than most cycle oils and this may have contributed to the high freeze point. One point of interest is the low smoke point (7.0 mm) on this sample. This is to be expected, since fuels this dense will have to be primarily composed of aromatics, rather than naphthenes.

Table 12  
HYDROTREATER/HYDROCRACKER JP-11 CANDIDATES

Refinery	Tentative		
	JP-11 Specs	Lion Oil	Texaco
Location (State)		Arkansas	Delaware
Stream Description		H/T LCO	H/C #2 Fuel Oil
Analyses			
API Gravity	< 25.7	24.9	29.7
Specific Gravity	> 0.900	0.9047	0.9348
Freeze Point, °F	<-51	-2	-45
Vis at -40°F, cs	< 40	Solid	61.9
Flash Point, °F	> 140	101	124
Smoke Point, mm	--	7.0	NA
JFTOT Results	Pass 260°C	NA	Pass
Sulfur, wt %	--	0.19	NA
D-86 Distillation, °F			
IBP/5 vol % over	360	296/415	269/395
10/20	--	445/472	425/453
30/40	--	487/503	475/491
50/60	--	516/529	505/523
70/80	--	544/561	542/564
90/95	--	587/596	599/633
EP	700	596	646
Structural Analysis, vol %			
Paraffins		21.7	NA
Cycloparaffins		9.2	
Di-cycloparaffins		5.2	
Tri-cycloparaffins		1.5	
Alkyl Benzenes		18.8	
Benzocycloparaffins		17.5	
Benzodicycloparaffins		6.7	
2-Ring aromatics		18.2	
Heavier aromatics + polars		1.2	
		100.0	

NA = Not analyzed

ND = None detected

H/T = Hydrotreated

H/C = Hydrocracked

LCO = Cat cracker light cycle oil

### Tosco Hydrocracker Recycle Stream

This sample, received from the Tosco Refinery, Avon, California, is from a product stream that is presently recycled back to the hydrocracker. This stream has previously been considered for jet fuel production but due to its low smoke point (16.0) and the lack of a good paraffinic blending stock, the stream is recycled and converted to gasoline, propane, and butane, as shown in Figure 4. The sample meets all the JP-8X specs except freeze point, being 5°F high. Discarding about 5% off the heavy end may help the freeze point but will also decrease the density, which is already marginal (37.2°API). The freeze point does not appear to be due to a high paraffin content since the mass spec analysis (Table 11) shows only 4.7% paraffins. Rather, this freeze point may be typical of highly saturated hydrocracker product and may mean that all such streams will require blending.

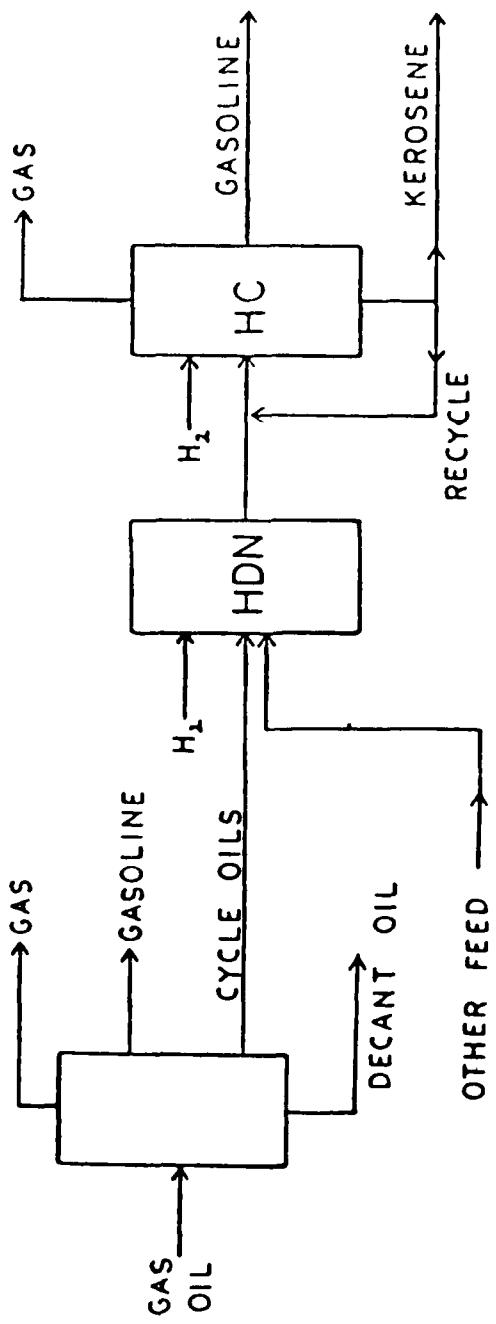
The present rate of this recycle stream is 8000 Bbl/day. The establishment of a market for JP-8X would immediately make this stream available, providing the economics were favorable.

### Tosco Hydrocracker Intermediate Stream

This sample was also received from the Tosco Refinery at Avon, California. This sample, and the Shell Oil sample discussed later, prove that hydrocrackers have the potential to produce JP-8X far in excess of foreseeable military requirements. Since hydrocracking is a two-stage operation, and since actual cracking is not desired to produce kerosene range material, the first stage (severe hydro-treating) may be the only step required to produce JP-8X. The intermediate stream or "HDN product/Isocracker feed" from the Tosco refinery confirms this. As shown in Table 11, the sample meets all specs easily except for the flash point. The flash point can be adjusted by distilling about 5% off the front or possibly by a stripping process, and this should not have much effect on the density. As shown by the mass spec analysis, this sample contains more paraffins and more aromatics than the recycle stream described above, and yet it has a better freeze point and smoke point.

This intermediate stream is essentially equal in size to the feed capacity, or 20,000 Bbl/day. Thus, if all U.S. hydrocrackers are similar in feedstock and operation to the Tosco hydrocracker (Chevron licensed Isocracker) as much as 1.07 mm Bbl/day of JP-8X could be produced. Tapping these streams will probably involve some refinery modifications and investments, but the feedstock and the process are essentially in place. Figure 5 shows the hydrocracker modification needed to maximize high density jet fuel production.

FCC



HYDROCRACKER

FIG. 4

NORMAL HYDROCRACKER CONFIGURATION

FCC      HYDROCRACKER

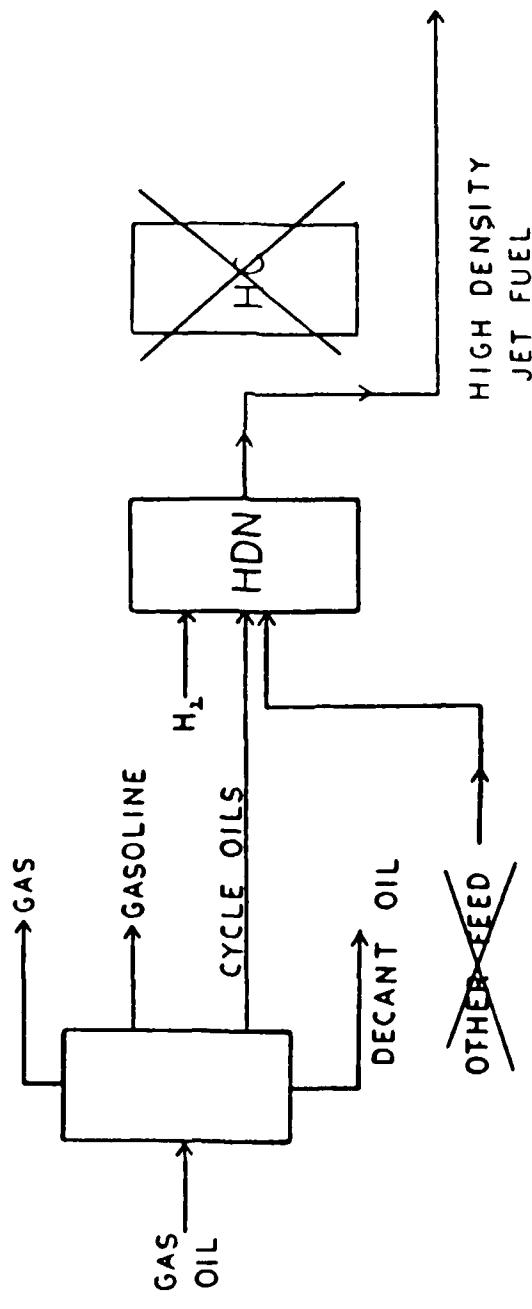


FIG. 5

HYDROCRACKER MODIFICATION TO MAXIMIZE JP-8X PRODUCTION

### Shell Hydrocracker Intermediate Stream

This sample, from the Shell refinery at Martinez, California is the only sample to pass all JP-8X specs, as received. Like the Tosco sample above, this material is first-stage product and second stage feed, but this stream has already been fractionated into the desired jet fuel boiling range. This was done because the Shell second stage reactor has been altered from a cracking reactor to an aromatics saturation unit. As such, the 2nd reactor will not significantly alter the boiling range, but will decrease the density as aromatics are changed to naphthenes. Saturation reactor conditions are much less severe than for hydrocracking, so the product rate of jet fuel from the second reactor can be essentially equal to the feed input of the first reactor. A second stage product sample was not obtained, but it is known that this stream is about 39°API and is sold to the U.S. Navy as JP-5, without requiring any blending to meet smoke point specs. Figure 6 illustrates this Shell hydrocracker modification.

The Shell process proves the flexibility of hydrocrackers. By having two reactors (or two stages) and by varying operating conditions and catalysts, hydrocrackers can be made to produce almost all gasoline, high density jet fuel, or, as in Shell's case, conventional jet fuel. The Shell process also provides a route by which jet fuels can be gradually made more dense with time, i.e., the saturation process can provide an interim kerosene type fuel, and as required, this saturation process can be bypassed to provide denser fuel. The Shell hydrocracker uses Shell 424 H/T catalyst in the first stage, and Shell 614 saturation catalyst in the 2nd stage.

Although the Shell hydrocracker has a 20,000 Bbl/day capacity, the intermediate stream is presently only about 10,000 Bbl/day. It is not known whether the unit is running below capacity or whether part of the intermediate stream is diverted elsewhere, such as to a diesel pool.

The analysis of hydrocracker samples resulted in an unexpected finding. It had been assumed that the most highly naphthenic samples would have the best combination of density, low temperature characteristics, and combustion characteristics. However, hydrocracker samples with roughly equal amounts of naphthenes and aromatics appeared to have better JP-8X properties than a highly naphthenic sample, as shown below.

	Tosco Recycle	Tosco Intermediate	Shell Intermediate
*API Gravity	37.2	33.5	34.6
Freeze Point, °F	-46	<-55	<-55
Vis at -40°F, cs	10.2	14.5	7.7
Smoke Point, mm	16.0	17.5	16.2
Components, Vol % by MS			
Paraffins	4.7	10.0	15.1
Naphthenes	73.5	53.0	40.2
Aromatics	21.8	37.0	44.7

FCC      HYDROCRACKER

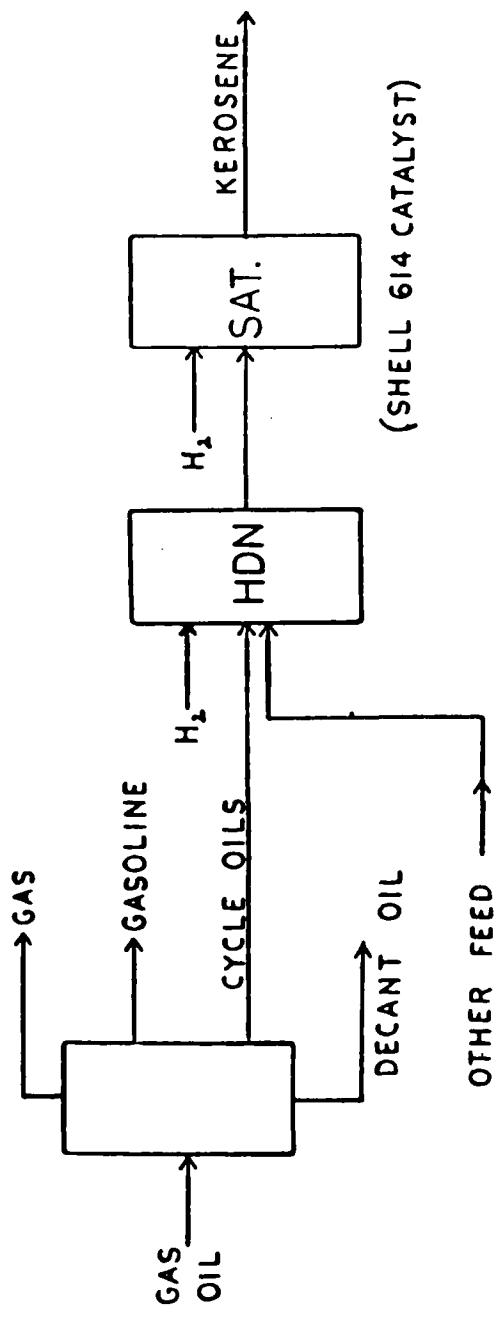


FIG. 6  
SHELL PROCESS TO MAXIMIZE JP-5 PRODUCTION

## Section VI

### Conclusions

#### A. Potential Availability of High Density Jet Fuel

Table 13 shows that JP-8X could be produced at a rate greater than present military and civilian consumption of kerosene type jet fuels, by utilizing the sources described below.

##### JP-8X From Naphthenic Crudes

Potential JP-8X from only the most naphthenic crude oils is estimated at 180,000 Bbl/day. These crudes produce such dense JP-8X fractions, that conventional streams can be blended in to stretch supplies. The prime blending crude appears to be Alaskan North Slope which is a moderately naphthenic crude. ANS is produced at the rate of 601 MM Bbl/year with proven reserves of 7393 MM Bbl. Production of straight-run ANS JP-8X boiling range material is 300,000 Bbl/day, but probably only 130,000 Bbl/day could be blended in. (50 % ANS distillate, 50% California crude distillate). Such blending could double the JP-8X potential production to 360,000 Bbl/day, or more than enough for military consumption which is around 300,000 Bbl/day.

##### Hydrocracker Product as JP-8X

The potential hydrocracker product that can be used as JP-8X is more difficult to gauge. Presently, it is estimated that around 30% of total hydrocracker product is a kerosene range product and that about half (170,000 Bbl/day) qualifies or nearly qualifies as JP-8X. However, by changing hydrocracker operating conditions or tapping hydrocracker intermediate streams, the product slate could be changed to yield essentially all jet fuel range material. J & A Associates estimates that only 80% of this product would qualify as JP-8X, resulting in a total potential JP-8X rate of 850,000 Bbl/day. However these hydrocracker estimates are based on limited samples, taken at one point in time, rather than long term or historical data. Producing a detailed estimate, projecting future scenarios, and evaluating economic implications were all outside the scope of this study.

#### B. Future Availability of JP-8X

Future supplies of JP-8X from naphthenic crude oil appear to be excellent. The highly naphthenic crudes have a higher ratio of reserves to production (12.8) than all U.S. crudes (8.7). The prime blending crude, ANS, has a reserve to production ratio of 12.3. Apparently, these crudes will be available for a longer time than the more conventional U.S. crude oils.

Hydrocrackers use primarily cycle oils from the catalytic cracking, or FCC, process as feedstock. This material is generated at over 1 MM Bbl/day, regardless of the type or origin of the crude brought into the refinery. As long as crude supplies are available, FCC cycle oils will be available, and the potential for producing high density jet fuel exists.

Table 13  
ESTIMATE OF AVAILABLE HIGH DENSITY JP-8 (JP-8X)

<u>Naphthenic Crudes(1)</u>			
<u>State</u>	<u>Annual Production</u>	<u>% SR Jet Fuel</u>	<u>Potential HD Jet Fuel</u>
Calif.	311.1 MM Bbl	15	46.7 MM Bbl/year
Texas	41.2 MM Bbl	35	14.4 MM Bbl/year
Louis. Ark.	14.6 MM Bbl	25	3.7 MM Bbl/year
	<u>366.9 MM Bbl</u>		<u>64.8 = 0.18 MM Bbl/day</u>
Alaskan S.R. as blending stock			= 0.13 MM Bbl/day
Other crude streams as blending stock			= 0.05 MM Bbl/day
Total S.R. JP-8X			<u>= 0.36 MM Bbl/day</u>

<u>Hydrocracker Product(2)</u>			
<u>Operating US Hydrocrackers</u>	<u>Total Capacity</u>	<u>Estimated Present Jet Fuel + Diesel</u>	<u>Potential HD Jet</u>
37	1.07 MM Bbl/day	0.3 MM Bbl/day (about 50% = JP-8X)	0.85 MM Bbl/day <sup>(3)</sup>

Total potential for HD kerosene type jet fuel	1.21 MM Bbl/day
1985 U. S. Consumption of kerosene type jet fuel	~1.0 MM Bbl/day
1985 U. S. Military consumption only	~0.3 MM Bbl/day

- (1) Estimate on naphthenic crudes based on a literature search of over 9,000 U.S. crudes and extensive analysis of 7 crude samples.
- (2) Estimate on hydrocracker production based on data from the Oil and Gas Journal and the analysis of samples from 10 U.S. hydrocrackers.
- (3) Assuming that essentially all H/C operations maximize jet fuel production.

### C. Possible Problems in Converting to JP-8X

Assuming that JP-8X causes no problems in present jet engines, a gradual changeover to JP-8X should cause no disruptions. Altering the hydrocracking process to yield primarily JP-8X may require some refinery investment and modifications, but the process is in place, and is proven.

An abrupt change in hydrocracker yield from primarily gasoline to primarily JP-8X could cause disruptions in the gasoline market. Presently hydrocrackers produce over 800,000 Bbl/day of gasoline (or gasoline precursor streams), which is 12% of U. S. consumption. This shortfall can be only partially offset by increasing FCC (catalytic cracker) throughput. Also, since demand for conventional straight-run jet fuels will drop, an excess of kerosene and diesel may develop.

Using naphthenic crudes for JP-8X production should not cause any disruption. The more paraffinic distillates would be used primarily for diesel fuel instead of jet fuel, leaving naphthenic distillates for jet fuel. This allows the best use of both crude oil types, since naphthenic crude produces an inferior diesel cut.

The main problem with naphthenic crudes is the isolation of those crudes, that is, preserving the identity of the crude during production, shipment, and refinery processing. This can be a major problem in the Gulf Coast area where naphthenic fields are small and surrounded by more conventional crude oils. In California, especially in the San Joaquin Valley, this may not be a problem. Also, in California, ANS crude (which makes an ideal blending stock) is the crude most often processed along with naphthenic California crudes.

### D. Quality of High-Density Fuels

JP-8X both from naphthenic crudes and from hydrocracker streams can meet the tentative JP-8X specs listed in Table 1. The properties examined compare favorably with the U.S.S.R. high density fuel and the high density fuel prepared by hydrotreating light pyrolysis oil and light cycle oil. For comparison, Table 14 and Figures 7 and 8 give J & A Associates analyses performed on the U.S.S.R. sample and on Sun Oil hydrotreated LCO's. These analyses were performed as part of this program in order to assess inter-laboratory reproducibility.

Tests for long-term stability, lubricity, surface tension, etc. were outside the scope of the program. Setting those specifications may limit the availability of JP-8X. Also, nothing is known about the combustion characteristics of these fuels in actual engines. This may again limit JP-8X availability if, for instance, a maximum aromatic content or minimum hydrogen content spec is required.

All efforts to produce a fuel that meets tentative JP-11 specs were unsuccessful. It appears impossible to meet both density and low temperature specifications by using either naphthenic crudes or hydrocracker streams as a JP-11 source. Relaxation of the density spec to 30°API (0.876 g/cc) may allow some of the samples examined to qualify as a marginal JP-11.

Table 14  
J & A ANALYSIS OF EXTERNALLY GENERATED JP-8X SAMPLES

<u>Analysis</u>	<u>USSR, Project Stablemate(1)</u>	<u>Sun Oil Marcus Hook DRS 489</u>	<u>Sun Oil Marcus Hook DRS 486</u>
*API Gravity	36.3	33.5	34.9
Smoke Point, mm	NA	19.1	19.4
Freeze Pt, °F	-90*	-42	-43
Flash Pt, °F	100*	128	129
Vis at -40°F	NA	9.49	9.10
Total Sulfur, wppm	8*	23	36
D-86 Distillation, °F			
IBP/5 Vol % over	187/368	318/342	311/347
10/20	412/443	358/376	360/376
30/40	461/475	385/401	388/403
50/60	487/499	415/435	417/433
70/80	512/525	451/477	451/480
90/95	546/560	525/572	520/583
EP, °F/ EP, vol %	568/98%	615/98%	617/98
Mass Spec Analysis, vol %			
Paraffins	25.2	14.5	15.8
Cycloparaffins	17.1	18.7	22.1
Dicycloparaffins	41.0	35.5	40.5
Tricycloparaffins	10.8	4.2	4.2
Alkyl Benzenes	3.6	14.3	9.3
Benzocycloparaffins	1.6	7.5	3.7
Benzodicycloparaffins	0.3	1.5	1.5
2-Ring Aromatics	0.4	2.2	1.8
Larger Aromatics	--	1.0	1.1
TOTAL	100.0	100.0	100.0

(1) Wright Patterson AFB #83-POSF-1028, December 16, 1976.  
 \* Exxon analysis.

MASS SPECTRUM  
01/20/66 17:04:00 + 17:30  
SAMPLE: RUSSIAN JET FUEL  
VOLUME: 0.1 UL  
#1, 15 #1430 SUMMED

DATA: USSRBA70 0760  
CALL: HAT7FAST 02

BASE M/E: 41  
RIC: 295305CJ.

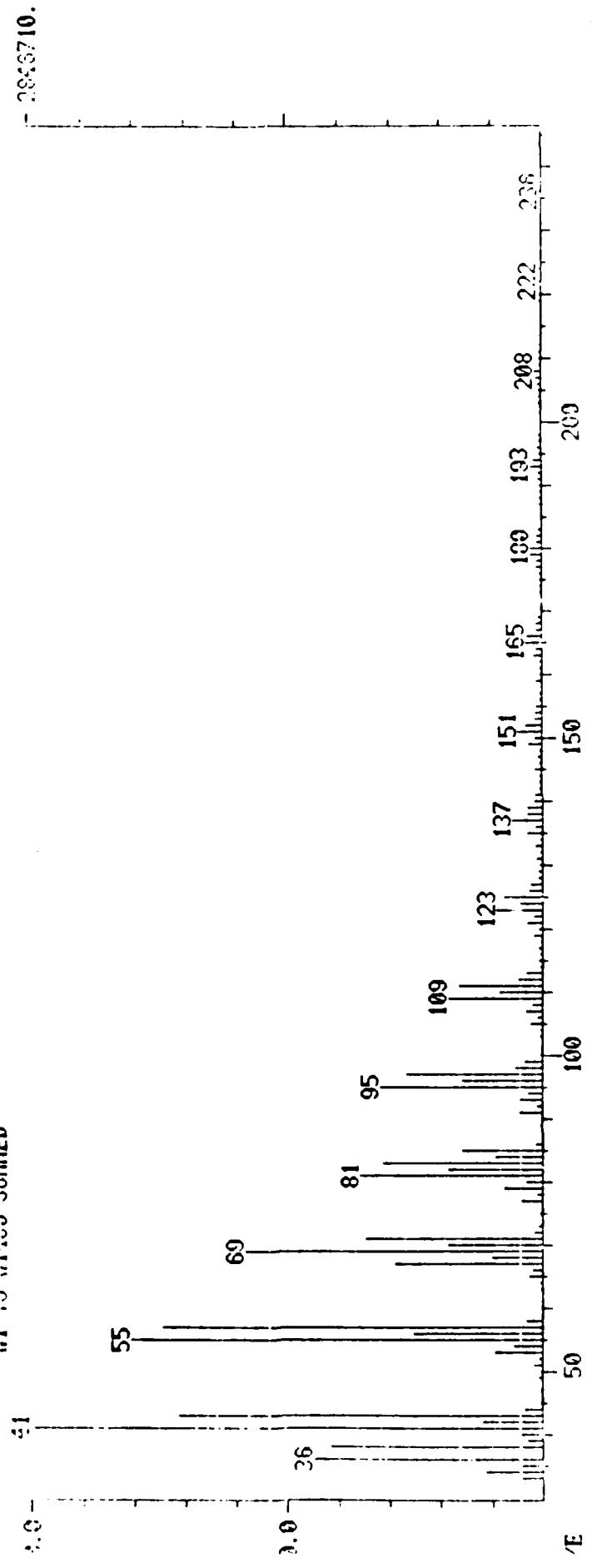
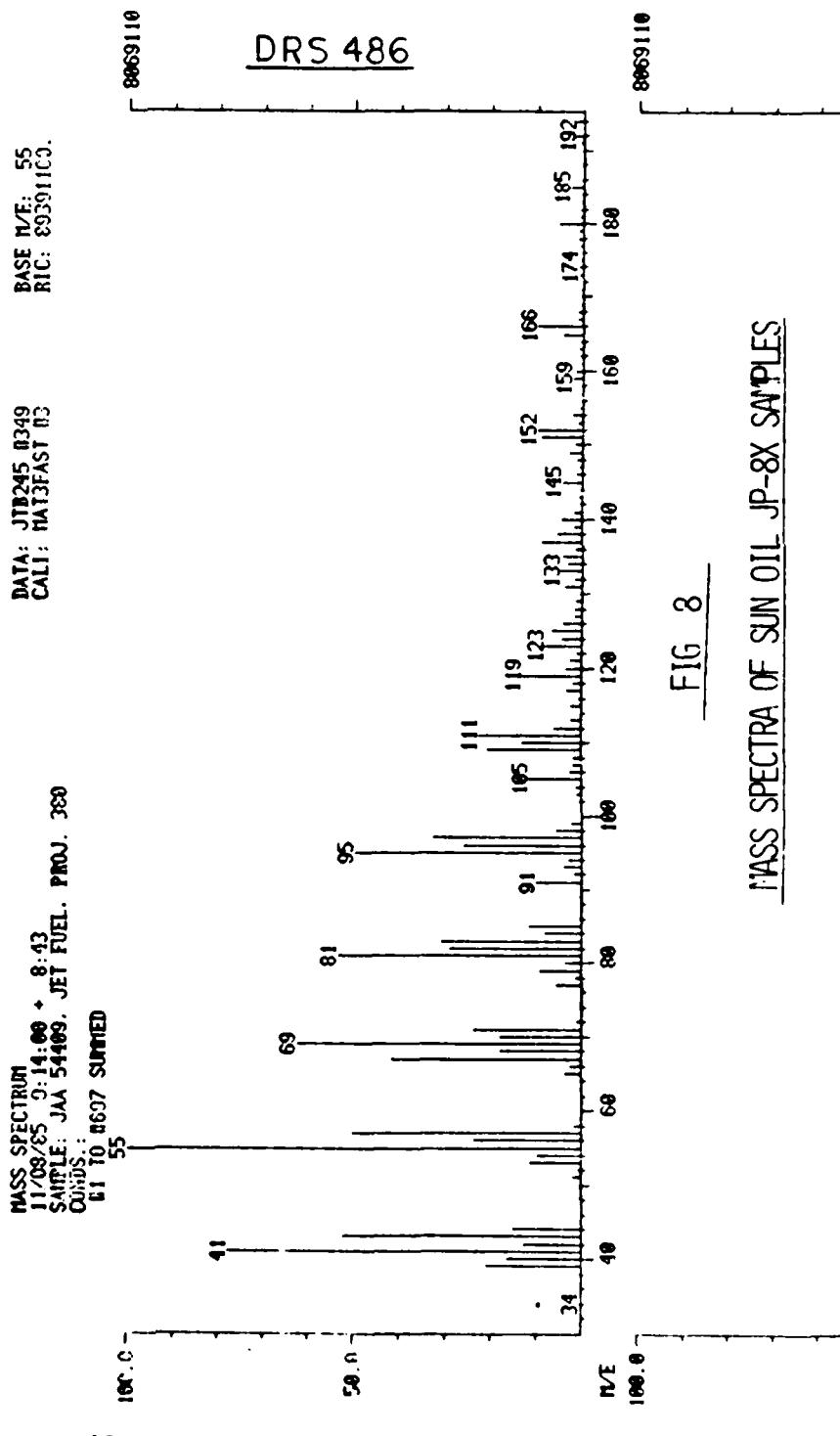
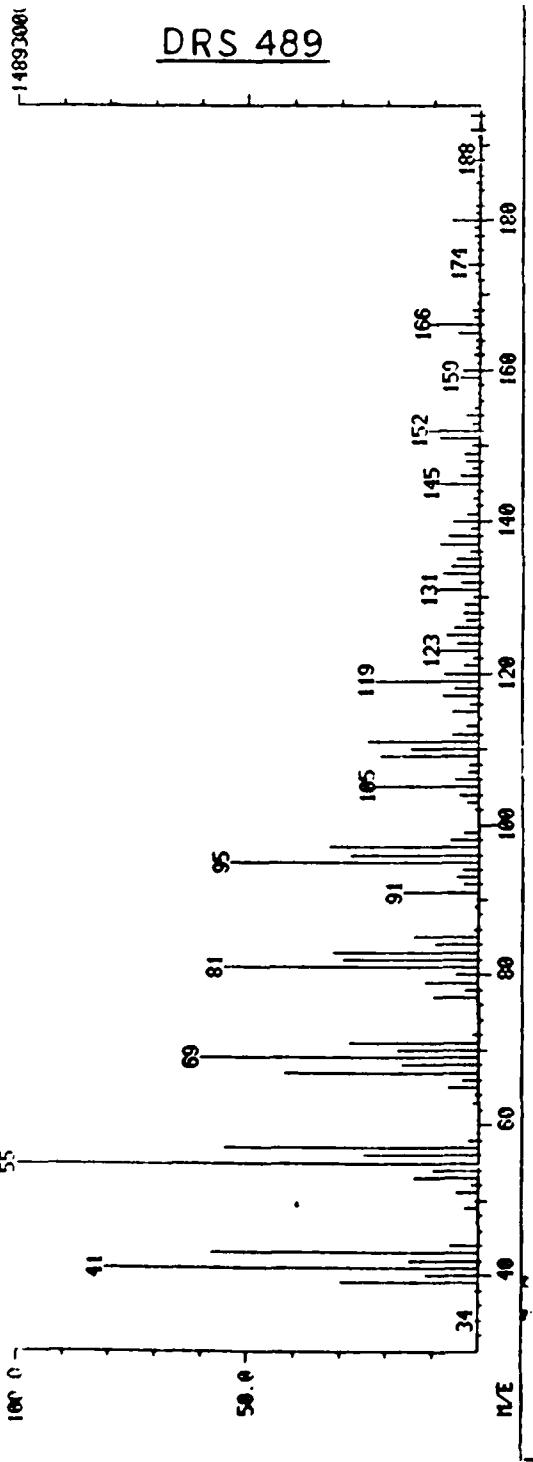


FIG. 7

MASS SPECTRUM OF U.S.S.R. JP-8X



MASS SPECTRA OF SUN OIL JP-8X SAMPLES

FIG 8

## Section VII

### Recommendations

Based on the findings in this study, additional work is recommended to more accurately assess the availability and quality of potential high density jet fuel.

- A. A crude oil survey of major import crudes should be conducted in order to determine foreign availability of naphthenic crudes. Samples would be procured, fractionated, and evaluated as JP-8X. Limited upgrading (hydrotreating, clay treating) would be conducted on selected samples.
- B. Large samples (1000 Bbls) of present streams that meet JP-8X specs should be procured and submitted for engine testing. The best candidates appear to be:
  1. Shell (Martinez) hydrocracker intermediate stream
  2. Texaco (Port Arthur) Manvel Crude straight-run
  3. Tosco (Avon) hydrocracker recycle stream
  4. Texaco (Delaware City) hydrocracker #2 fuel oil
  5. Tosco (Avon) hydrotreated SJV/ANS straight-run  
(Samples 4 and 5 would require re-distillation).
- C. Additional analyses and long term storage tests should be conducted on the samples obtained in this survey. These analyses would consist of lubricity, gum content, heating content, elemental analysis, surface tension, neutralization number, and mass spec analysis, if not already performed. A second set of samples should be obtained in about six months to determine stream or crude variability.
- D. Additional hydrotreating tests should be performed on the California crudes (San Ardo, Beta, SJV) in order to determine the minimum treatment required. An evaluation of the latest H/T catalysts could be part of this study. These data are needed because the California crudes are the largest naphthenic crude resource but cannot be used for jet fuel without significant upgrading.
- E. The variability of light cycle oils and the impact on JP-8X quality should be examined. Three LCO's from different geographic locations and originating from different crudes should be hydrocracked in a pilot plant. A second part of this study could be to evaluate aromatics saturation catalysts such as Shell 614. This study could make JP-8X production by hydrocracking a more predictable process.
- F. A more comprehensive refinery search should be conducted to find and quantify internal naphthenic streams that could be used as JP-8X. Many such streams should exist in California, but refineries with lube or asphalt plants may also contain such streams.
- G. The tentative JP-11 specifications will have to be altered. The density and low temperature specs appear to be mutually exclusive.

## References

1. C. L. Delaney, Air Force Wright Aeronautical Laboratories, Presentation at a High Density Jet Fuel Analysis Workshop, Golden, Colorado, November 14, 1985.
2. A. Korosi, J. N. Rubin, Stone and Webster Engineering Corp, "Hydroprocessing of Light Pyrolysis Fuel Oil for Kerosene Type Jet Fuel," USAF Technical Report, AFWAL-TR-80-2012, Feb, 1980.
3. L. W. Hall, H. E. Reif, Sun Refining and Marketing Co., "Production of High Density Fuel Samples," work in progress, USAF contract DLA600-85-C-0497, presentation at High Density Jet Fuel Analysis Workshop, November 14, 1985.
4. G. P. Hammer, Exxon, "Hydrogenation of Aromatic Distillates (LCCO)," work in progress, presentation at High Density Jet Fuel Analysis Workshop, November 14, 1985.
5. E. B. Smith, Western Research Institute, Hydrotreating Tests in Progress, presentation at High Density Jet Fuel Analysis Workshop, November 14, 1985.
6. H. Shaw, C. E. Kalfadelis, C. E. Jahnig, Exxon Research and Engineering Co., "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils,"- Phases I-III USAF Technical Report AFAPL-TR-75-10, Vol I-III, 1975-1977.
7. H. F. Moore, Ashland Petroleum Co., "Jet Fuel Production from Tar Sands and Heavy Oil," by ART/Reduced Crude Conversion Process', March 26, 1985.
8. A. F. Talbot et. al., Sun Refining and Marketing Co., "Jet Fuel Production from Tar Sands Bitumen via Hydrovisbreaking, Hydrotreating, and Hydrocracking," March 26, 1985.
9. Ashland Petroleum Co., work in progress, "Phase II Objectives," USAF Contract F33615-83-C-2301, March 26, 1985, presentation.
10. Oil and Gas Journal, September 9, 1985.

**APPENDIX A**  
**STATEMENT OF WORK**

STATEMENT OF WORK  
Subcontract G-9046 (8827)-544, Battelle-Columbus

TASK TITLE: High Density Jet Fuel Supply and Specification

TASK OBJECTIVE: The objective of this task is to perform a quick survey of domestic crude oils which may provide an adequate straight-run high density jet fuel; and to provide a comprehensive search for refinery intermediates which could constitute a high-density jet fuel or an easily processed precursor stream.

TASK DESCRIPTION: In order to increase the range of military aircraft, high-density kerosene type jet fuels are being considered by the USAF. Fuel density is determined by molecule size and type and can only be altered by chemical processes. Therefore, high-density fuel will require tapping different hydrocarbon sources or product streams than are presently used. This task consists of two parts and are delineated below:

Part I - Straight-Run (Virgin) Fuel From Naphthenic Crudes. The researcher shall identify ten candidate naphthenic crudes as well as the availability and geographic distribution. The researcher will procure samples of the crude and refinery straight-run product, if available. The procurement samples are to be fractionated on a true boiling point (TBP) apparatus, taking cuts at 360° - 520°F and 360° - 700°F. The samples will be screened by analyzing each fraction for API gravity and specific gravity, viscosity at -4°F and freeze point. Of the three best samples in the 360° - 520°F fractions the researcher will perform ASTM D1655 Aviation Turbine Fuel Specification Tests (Jet A) for total sulfur, smoke point, flash point, D-86 distillation. In addition, mass spectral analysis for complete structural identification will be performed.

The researcher will evaluate all analyses on the three samples; compare the results with the Jet A specifications and make recommendations on how the failed tests could be passed (i.e., adjustments in hydrotreating, blending, different cut points and/or other chemical processing).

Part II - Light Cycle Oil Derived Jet Fuel. The researcher shall perform a refinery survey, locating and determining availability of hydrotreated, hydrocracked light cycle oil cuts at 360° - 520°F. After the survey, ten best candidate sample products with the following characteristics will be selected: a) total hydrotreated or hydrocracked liquid product and b) fractions within the required jet fuel boiling range. If the ten product samples do not fall within the desired boiling range of 360° - 520°F and 360° - 700°F, a TBP distillation will be performed to obtain the desired boiling range fractions. Both fractions will be screened by analyses for API gravity, specific gravity, viscosity @ -4°F and freeze point. After screening the samples in the 360° - 520°F range, the three best candidate samples will be further analyzed by ASTM D1655, (Jet A) for total sulfur, mercaptan

sulfur, smoke point, flash point and D-86 distillation. In addition, mass spectral analysis for complete structural identification will be performed.

The researcher will evaluate all analyses on the three samples; compare the results with the Jet A specifications and make recommendations on how the failed tests could be passed (i.e., adjustments in unit feedstocks, blending, hydrotreating, and hydrocracking).

**REQUIRED REPORTING:** 1. (TOR) Technical Operating Report DI-S-30559M\*. This report will cover all aspects of the task, especially analyses, comparisons and recommendations. 2. Regular telecommunications with government focal point.

Schedule (Desired start/stop dates):	01 May 85 - 30 Sep 85
Estimated Researcher Hours:	700
Recommended Researcher:	Dr Mark T. Atwood (303) 425-6021
Location of Effort:	J and A Associates, Inc. 18200 West Highway 72 Golden CO 80401
Government Focal Point:	C.L. Delaney (513) 255-2460 H.R. Lander (513) 255-4027 AFWAL/POSF Wright-Patterson AFB OH 45433-6563

This is Task #4 of contract F33615-84-C-2410 (BAT)

**APPENDIX II**

**TRUE BOILING POINT DISTILLATIONS ON**

**NAPHTHENIC CRUDE OILS**

DISTILLATION REPORT

Dist. Type: TBP  
011 No. 3-6889  
011 Source: SJV Pipeline Crude From Tosco, Avon Refinery

Cut Number	Dist. Range F at Atm.	Wt (g)	Weight (g)	≤ Weight %	Specific Gravity	*API	Vol. (ml)	Vol. %	≤ Vol. %
1	< 200°F (C. T. mat.)	67.4	0.76	0.76	.7426	59.1	90.8	1.00	1.00
2	300-360	30.0	0.34	1.10	.7884	48.0	38.1	0.42	1.42
3	360-475	424.7	4.78	5.88	.8537	34.3	497.5	5.45	6.87
4	475-591	809.9	9.11	14.99	.8946	26.7	905.3	9.93	16.80
5	591-700	992.3	11.16	26.15	.9312	20.4	1065.6	11.68	28.48
6	700-720	197.7	2.22	28.37	.9514	17.2	207.8	2.28	30.76
7	720-740	202.6	2.28	30.65	.9565	16.4	211.8	2.32	33.08
	Totals	2724.6	30.64				3016.9	33.08	
8	740+	6117.2	68.80	99.44	1.0087	8.8	6064.4	66.49	99.57
	Totals	8841.8					5081.3		

Notes:

Crude contained 38.6 g H<sub>2</sub>O; all results are reported on a dry basis.

Dry Charge: 8891.3 gms. 9121.2 mls. Charge Data: 8891.3 gms.  
Recovery: 8841.8 gms. 9081.3 mls. SG = 0.9748 API = 13.6°  
L & H: 49.5 gms. 39.9 mls. Residuum Data: 6117.2 gms.  
% Recovery: 99.44 % 99.56 % SG = 1.0087 API = 8.8°

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Page 11

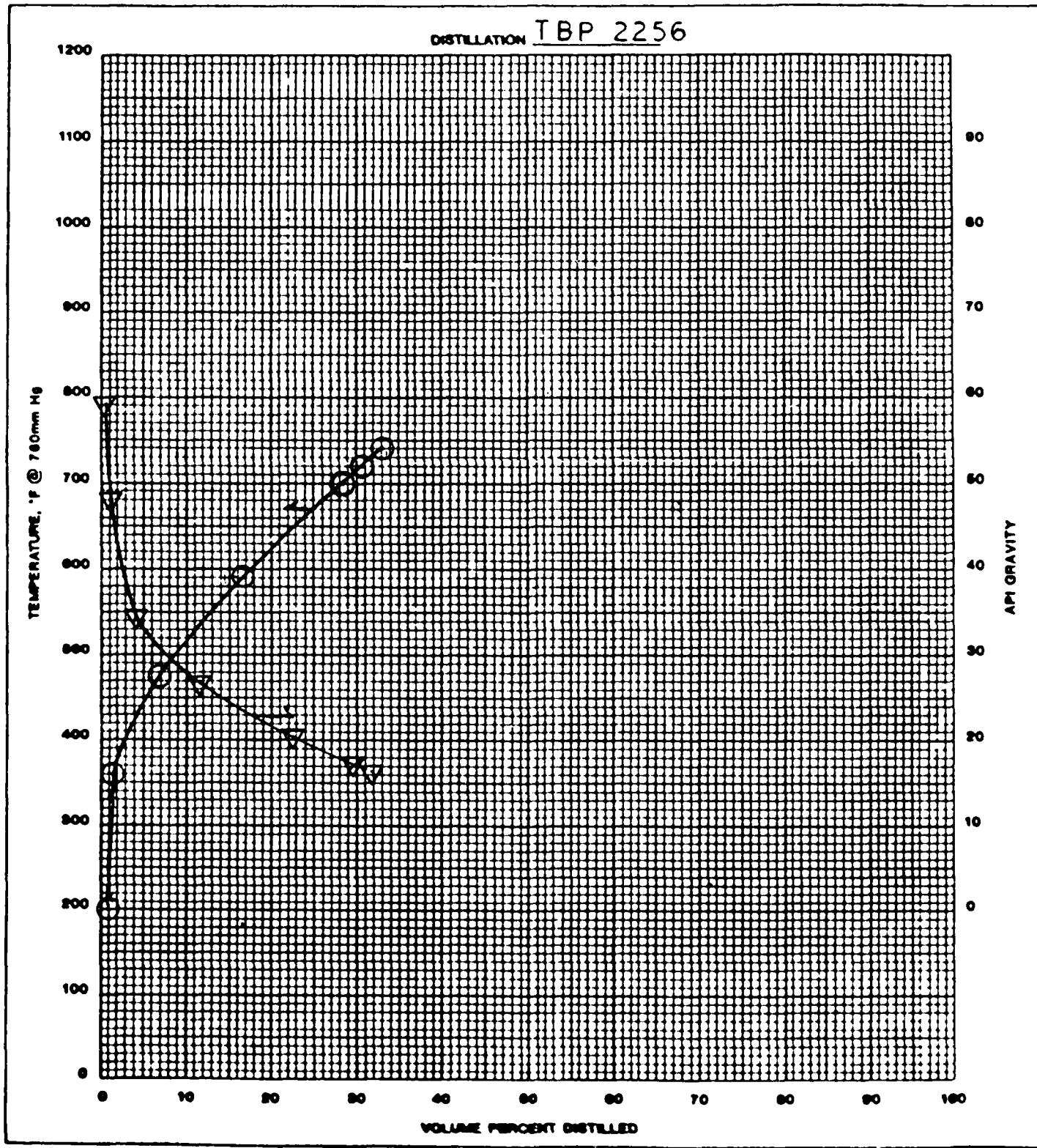
SUBJECT: SJV PIPELINE CRUDE FROM TOSCO PAGE \_\_\_\_ OF \_\_\_\_

AUTHOR: DATE: 5/14/85 PROJECT: \_\_\_\_\_

REF: 36889

ANALYST: C M Smith

DISTILLATION TBP 2256



DISTILLATION REPORT

Dist. Type: TBP  
011 No. 54759  
011 Source: Beta Crude From Shell Oil, Carson, California

Dist # 2265  
Proj # 380

Date Run 12/24/85

Analyst C. M. Smits

J & A	Dist. Range F at T Atm.	Wt. (g)	Weight <u>(g)</u>	% Weight <u>g</u>	Specific Gravity	* API	Vol. ml	Vol. g	% Vol. %
54759-A	TBP(105)-350	287.8	8.20	8.20	0.7546	56.0	381.4	10.42	10.42
54759-B	350-565	436.4	12.43	20.63	0.8610	32.8	509.6	13.85	24.27
54759-C	565-650	245.5	7.00	27.63	0.9067	24.6	270.8	7.40	31.67
	Total Overhead	959.7	27.63				1159.1		
54759-D	650+	2531.0	72.12	99.75	1.0092	8.7	2507.9	68.53	100.20
	Totals	3500.7	99.75				3667.0	100.20	

## Notes:

350-650°F = 0.8768 S.G., 29.9°API.  
Crude contained 75.5 g water or 2.11 weight % water. All results are reported on a  
dry basis.

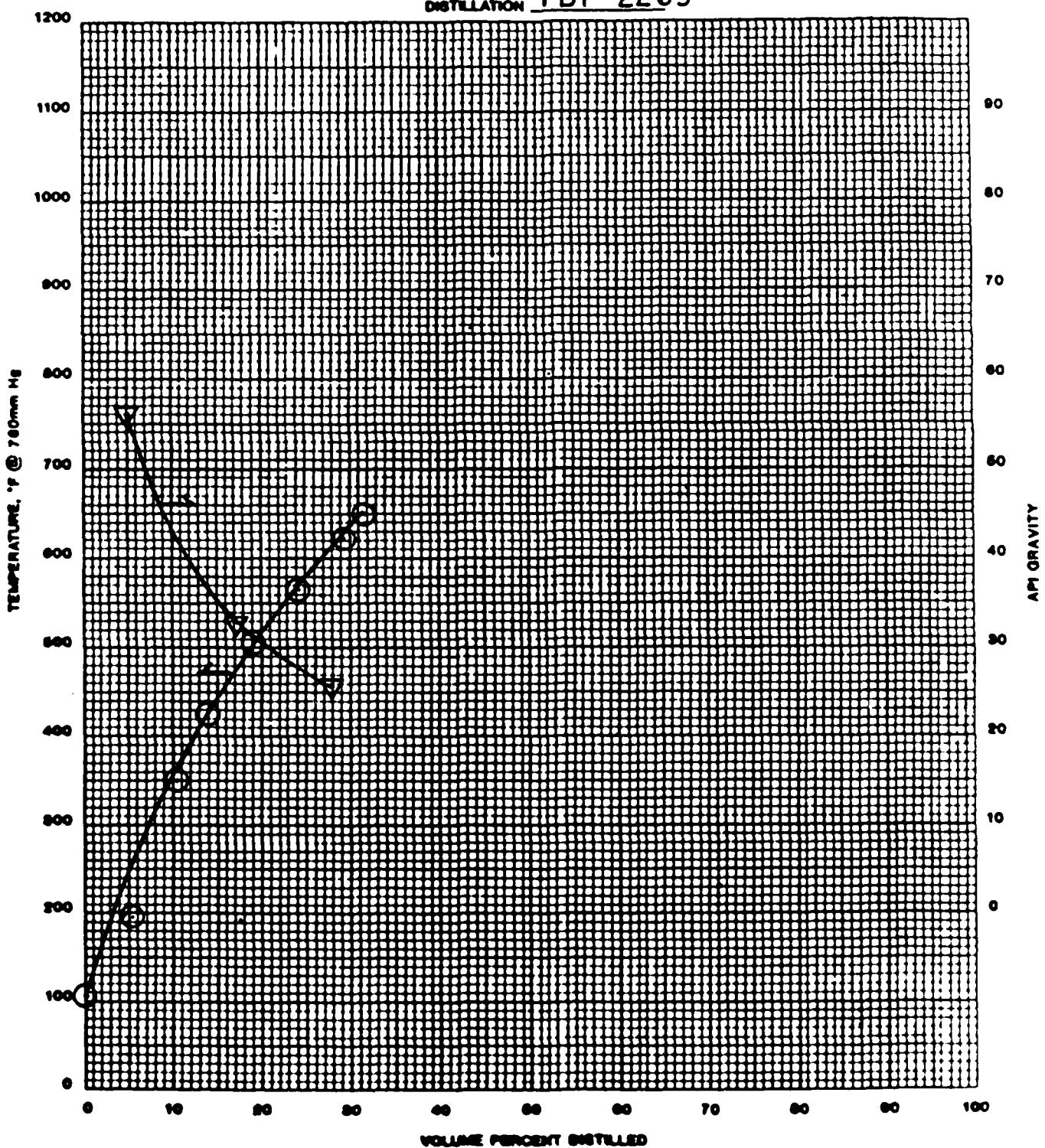
Dry Charge: 3509.5 gms. 3659.5 ml s. Charge Data: 3509.5 gms.  
Recovery: 3500.7 gms. 3667.0 ml s. SG = 0.9590 API = 16.1°  
L & H: 8.8 gms. (7.5) ml s. Residuum Data: 2531.0 gms.  
% Recovery: 99.75 % 100.20 % SG = 1.0092 API = 8.7°

SUBJECT: BETA CRUDE FROM SHELL OIL PAGE \_\_\_\_\_ OF \_\_\_\_\_

AUTHOR: \_\_\_\_\_ DATE: 12/24/85 PROJECT # \_\_\_\_\_

RF# 54759 ANALYST: C M Smith

DISTILLATION TBP 2265



DISTILLATION REPORT

Dist. Type: TBP/H1-Vac  
 011 No. J & A # 50216  
 Proj # 342  
 011 Source: San Ardo Crude From Texaco, Received 6/12/85

Dist. # 2259  
 Date Run 6/18/85  
 Analyst C. M. Smits

Cut	Dist. Range Fatt Atm.	Wt. (g)	Weight % <u>(g)</u>	% Weight <u>%</u>	Specific Gravity	*API 60/60	Vol. mls. <u>(mls)</u>	Vol. % <u>mls</u>	% Vol.
1	TBP(188)-250	18.0	0.21	0.21	0.7552	55.9	23.8	0.27	0.27
2	250-340	118.2	1.38	1.59	0.8011	45.1	147.5	1.68	1.95
3	340-380	106.5	1.24	2.83	0.8305	38.9	128.2	1.46	3.41
4	380-450	411.8	4.81	7.64	0.8604	33.0	478.6	5.46	8.87
5	450-550	698.3	8.15	15.79	0.8881	27.8	786.3	8.96	17.83
6	550-650	854.0	9.97	25.76	0.9144	23.3	933.9	10.65	28.48
7	650-750	544.0	6.35	32.11	0.9468	17.9	574.6	6.55	35.03
8	750-850	957.9	11.19	43.30	0.9560	16.5	1002.0	11.42	46.45
9	850-950	899.3	10.50	53.80	0.9747	13.7	922.6	10.52	56.97
10	950-1010*	674.5	7.88	61.68	0.9966	10.5	676.8	7.71	64.68
	Total Overhead	5282.5	61.68				5674.3	64.68	
11	1010+	3268.3	38.16	99.84	1.0502	3.2	3112.0	35.47	100.15
	Totals	8550.8	99.84				8786.3		
12	650+	6343.4	74.07	99.83	1.0122	8.3	6266.9	71.44	99.92
13	850+	4842.1	56.54	99.84	1.0275	6.2	4712.5	53.72	100.17

Crude contained 82.9 g or 0.96 wt % H<sub>2</sub>O. All results are on a dry basis.  
 \* Distillation halted due to the onset of thermal cracking.

Charge:	8563.8 gms.	8772.6 mls.	Charge Data: 8563.8 gms.
Recovery:	8550.8 gms.	8786.3 mls.	SG = 0.9762 API = 13.4°
L & H:	13.0 gms.	(13.7) mls.	Residuum Data: 3268.3 gms.
% Recovery:	99.85 %	100.16 %	SG = 1.0502 API = 3.2°

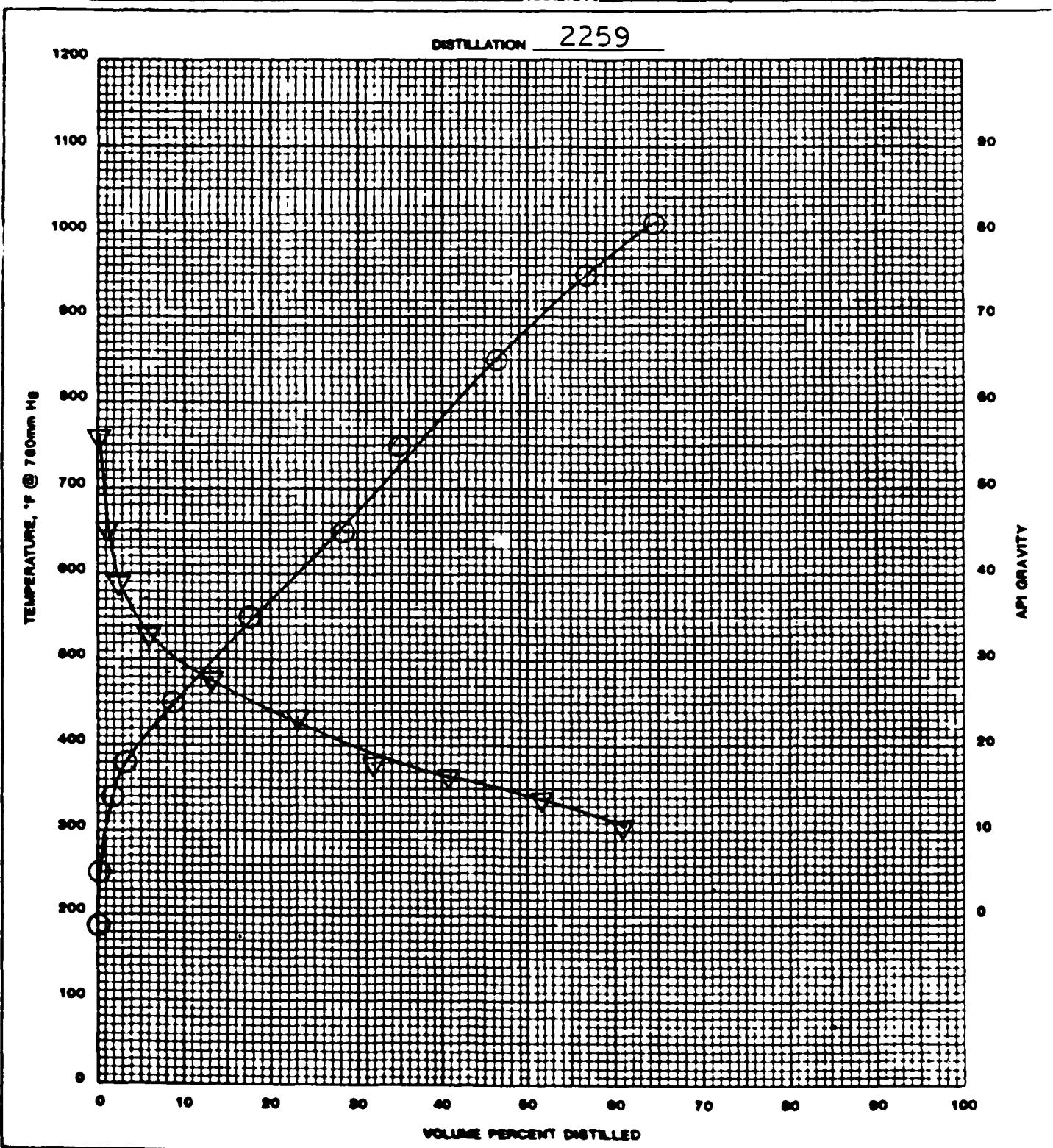
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SUBJECT: SAN ARDO CRUDE FROM TEXACO PAGE \_\_\_\_ OF \_\_\_\_

AUTHOR: \_\_\_\_\_ DATE: 6/18/85 PROJECT: \_\_\_\_\_

RF: J+A # 50216 ANALYST: C M Smith

DISTILLATION 2259



DISTILLATION REPORT

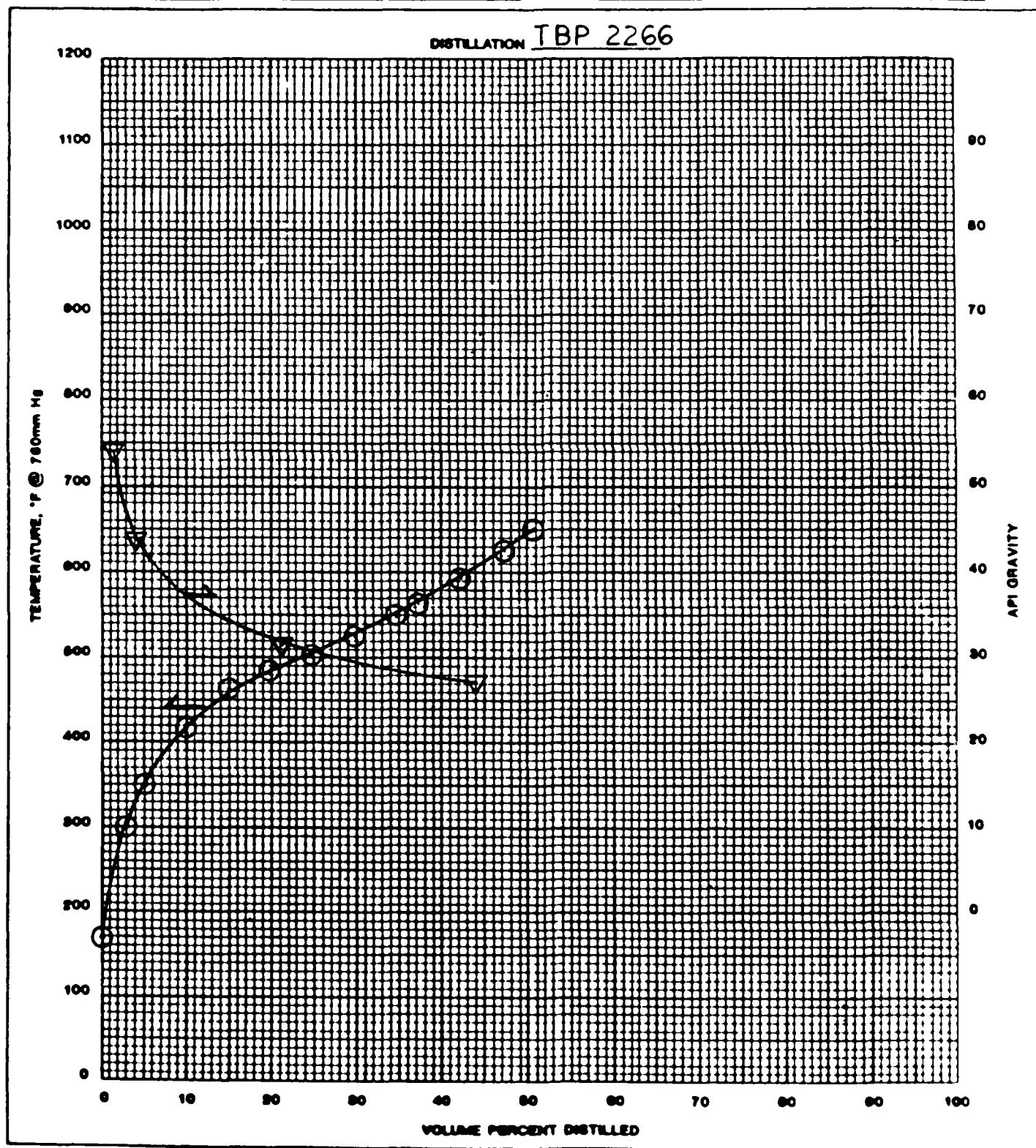
Dist. #	Type:	TBP Oil No.	Dist. # 2266 Source Manvel Crude Received From Texaco, Port Arthur, Texas	Date Run Proj # 380	Analyst	C. H. Smits
J & A	Dist. Range F at 1 Atm.	Wt (g)	Weight 2 g	Specific Gravity	Vol. ml	Vol. %
54736-A	IBP(169)-300	212.4	2.56	0.7638	53.8	278.1
54736-B	300-350	160.3	1.93	0.8067	43.9	198.7
54736-C	350-563	2589.4	31.23	0.8684	31.4	2981.8
54736-D	563-650	1110.3	13.39	0.8915	27.2	1245.4
Total Overhead		4072.4	49.11		4704.0	50.76
54736-E	650+	4196.0	50.60	0.9259	21.3	4531.8
Totals		8268.4	99.71		9235.8	99.67

Notes:

300-650°F = 0.8721 S.G., 30.8°API.  
Crude contained 13.5 g of water or 0.13 weight percent water.  
All results are reported on a dry basis.

Dry Charge: 8292.5 gms. 9266.4 ml s. Charge Data: 8292.5 gms.  
Recovery: 8268.4 gms. 9235.8 ml s. SG = 0.8949 API = 26.6°  
L & H: 24.1 gms. 30.6 ml s. Residuum Data: 4196.0 gms.  
% Recovery: 99.71 % 99.67 % SG = 0.9259 API = 21.3°

SUBJECT: MANVEL CRUDE FROM TEXACO PAGE \_\_\_\_\_ OF \_\_\_\_\_  
AUTHOR: \_\_\_\_\_ DATE: 12/24/85 PROJECT # \_\_\_\_\_  
RF: 54736 ANALYST: C M Smita



DISTILLATION REPORT

Dist. Type: TBP  
01 No. 54499  
01 Source: Refugio Crude 011 From Coastal States, Corpus Christi, Texas

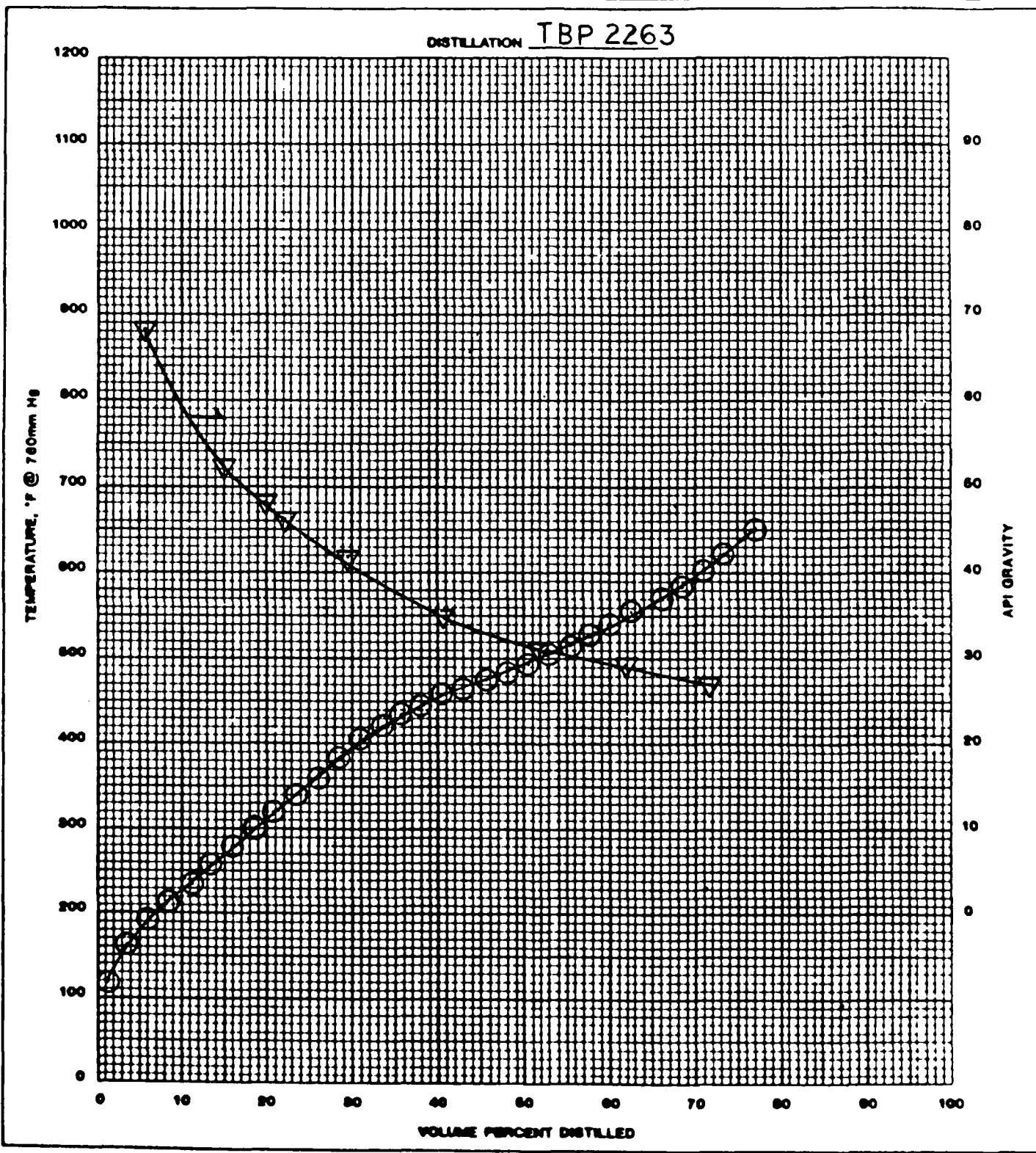
Dist # 2263  
Proj # 380  
Date Run 11/19/85  
Analyst C. M. Smits

Cut	Dist. Range Fat Atm.	Wt. (g)	Weight 1/2	Weight 1/2	Specific Gravity	*API 60/60	Vol. [ml]	Vol. %	% Vol.
54499-A	TBP-234	706.1	9.32	0.7085	68.2	996.6	11.29		
54499-B	234-300	500.4	6.60	0.7703	52.2	649.6	7.36	18.65	
54499-C	300-320	154.8	2.04	0.7879	48.1	196.5	2.23	20.88	
54499-D	320-340	183.4	2.42	0.7957	46.3	230.5	2.61	23.49	
54499-E	340-435	878.0	11.59	0.8171	41.7	1074.5	12.17	35.66	
54499-F	435-475	748.2	9.87	0.8507	34.8	879.5	9.97	45.63	
54499-G	475-528	929.1	12.26	0.8702	31.1	1067.7	12.10	57.73	
54499-H	528-570	646.2	8.53	0.8800	29.3	734.3	8.32	66.05	
54499-J	570-650	873.1	11.52	0.8919	27.1	978.9	11.09	77.14	
Total Distilled	5619.3	74.15				6808.1	77.14		
54499-L	650+	1947.1	25.69	0.9618	15.6	2024.4	22.94	100.08	
	Totals	7566.4	99.85			8832.5			
54499-I	340-570	3201.5	42.25	0.8524	34.5	3755.9	42.55	--	
54499-K	300-650	4412.8	58.23	0.8550	34.0	5161.2	58.48	--	

Charge: 7578.0 gms. Charge Data: 7578.0 gms.  
Recovery: 7566.4 gms. SG = 0.8586 API = 33.3°  
L & H: 11.6 gms. Residuum Data: 1947.1 gms.  
% Recovery: 99.85 % SG = 0.9618 API = 15.6°

Dist: CMSI  
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Page 14  
11/20/85

SUBJECT: REFUGIO CRUDE from COASTAL PAGE \_\_\_\_\_ OF \_\_\_\_\_  
AUTHOR: \_\_\_\_\_ DATE: 11/19/85 PROJECT # \_\_\_\_\_  
RF# 54499 ANALYST: C M. fonte



DISTILLATION REPORT

Dist. Type: TBP  
011 No. 48T26  
011 Source Smackover Pipeline Crude, Received from El Dorado 4/23/85

Cut	Dist. Range F Atm.	Wt. (g)	Weight ± %	Weight ± %	Specific Gravity	*API	Vol. [ml]	Vol. %	± Vol. %
1	TBP(106)-247(1)	344.0	4.17	4.17	0.7020	70.1	490.0	5.41	5.41
2	247-320	266.8	3.23	7.40	0.7668	53.0	347.9	3.84	9.25
3	320-340	95.8	1.16	8.56	0.7918	47.2	121.0	1.34	10.59
4	340-360	96.4	1.17	9.73	0.8020	44.9	120.2	1.33	11.92
5	360-380	91.1	1.10	10.83	0.8104	43.1	112.4	1.24	13.16
6	380-561	1252.1	15.18	26.01	0.8475	35.5	1477.4	16.32	29.48
7	561-660	878.8	10.65	36.66	0.8845	28.5	993.6	10.97	40.45
8	660-680	188.1	2.28	38.94	0.9077	24.4	207.2	2.29	42.74
9	680-700	176.6	2.14	41.08	0.9090	24.2	194.3	2.15	44.89
10	700-720	144.9	1.76	42.84	0.9095	24.1	159.3	1.76	46.65
11	720-740	143.3	1.74	44.58	0.9104	23.9	157.4	1.74	48.39
	TOTAL OVERHEAD	3677.9	44.59				4380.7	48.35	
12	740+	4546.3	55.12	99.71	0.9736	13.8	4669.6	51.58	99.97
	TOTALS	8224.2					9050.3		

Notes:  
(1) Includes 23.4 g dry ice trap material. Crude contained 0.11 % H<sub>2</sub>O,  
all data are reported on a dry basis.

Charge: 8248.7 gms. 9053.6 mls. Charge Data: 8248.7 gms.  
Recovery: 8224.2 gms. 9050.3 mls. SG = 0.9111 API = 23.8°  
L & H: 24.5 gms. 3.3 mls. Residuum Data: SG = 4546.3 gms.  
% Recovery: 99.70 % 99.96 % SG = 0.9736 API = 13.8°

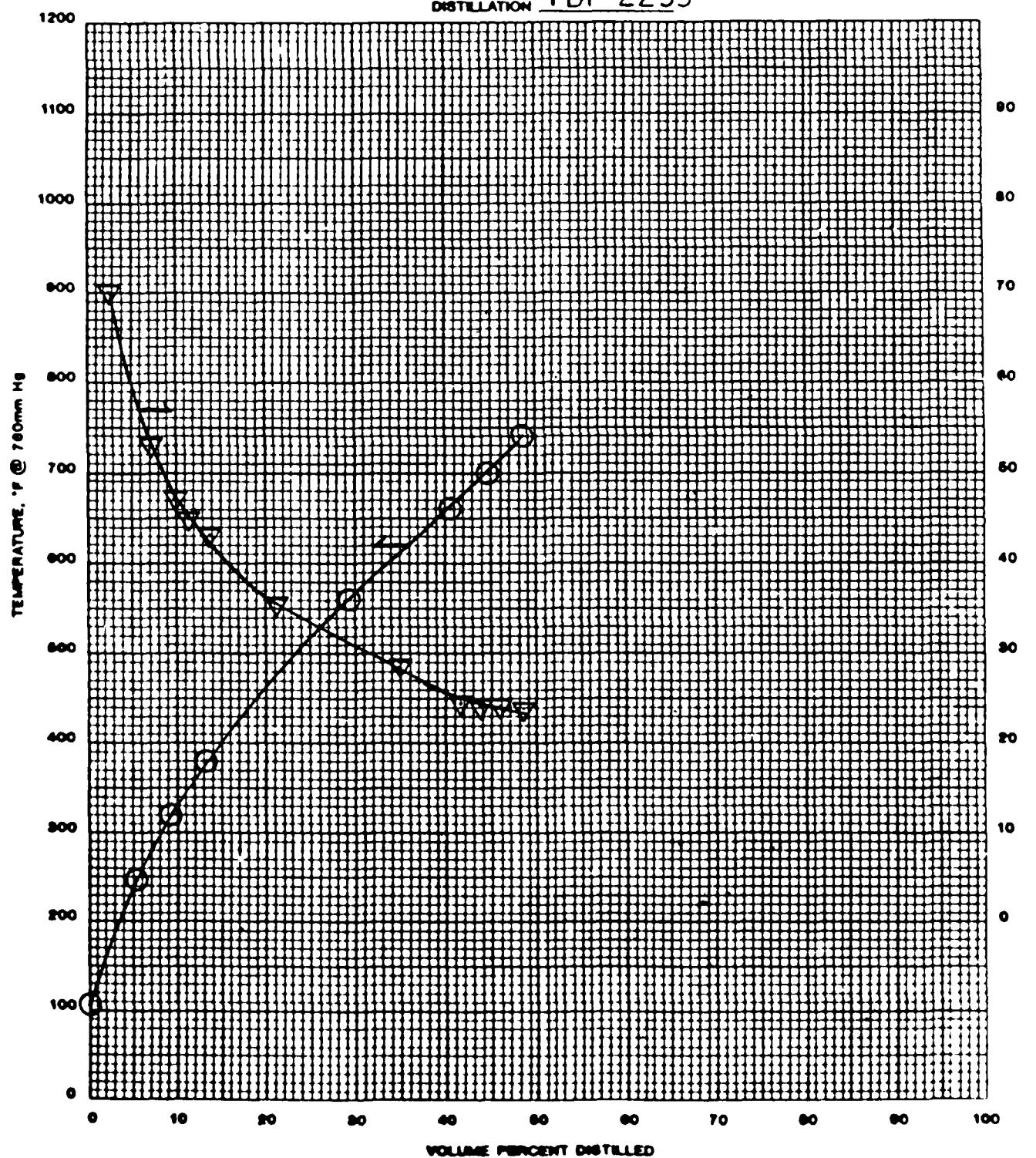
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Page 11

SUBJECT: SMACKOVER CRUDE FROM LION OIL PAGE        OF       

AUTHOR: \_\_\_\_\_ DATE: 5/7/85 PROJECT #       

RF# 48126 ANALYST: C M Smith

DISTILLATION TBP 2255



DISTILLATION REPORT

Dist. Type: TBP  
011 No. J & A # 48125  
011 Source: LAK Crude, Received From Surtek April 11, 1985

Cut	Dist. Range F at 1 Atm.	Wt (g)	Weight g	% Weight	Specific Gravity	API 60/60	Vol. ml	Vol. g	% Vol.
1	<75 (Cold Trap Material)	24.6	0.33	~0.600(1)	~104(1)	41.0	0.52	0.52	0.52
2	370-400	30.9	0.42	0.75	0.84988	35.2	36.4	0.46	0.98
3	400-583	873.6	11.77	12.52	0.8859	28.2	986.1	12.45	13.43
4	583-660	642.8	8.66	21.18	0.9085	24.2	707.5	8.93	22.36
5	660-680	192.4	2.59	23.77	0.9194	22.4	209.3	2.64	25.00
6	680-700	193.5	2.61	26.38	0.9235	21.7	209.5	2.65	27.65
7	700-720	206.0	2.78	29.16	0.9274	21.1	222.1	2.80	30.45
8	720-740	201.6	2.72	31.88	0.9304	20.6	216.7	2.74	33.19
Total	Overhead	2365.4	31.87				2628.6	33.19	
740+		5020.2	67.64	99.51	0.9582		5239.2	66.16	99.35
	Totals	7385.6				16.2	7857.8		

(1) Sample evaporated in the freezer before density measurement could be made.  
(2) 011 contained 7.18 wt % water; all results are reported on a dry basis.  
(3) L&H is primarily column hold-up. Normal hold-up in the 2" TBP is 40g.

Charge: (2) 7421.6 gms. Charge Data: (2) 7421.6 gms.  
Recovery: 7385.6 gms. SG = 0.9372 API = 19.5°  
L & H: (3) 36.0 gms. 51.1 mls. Residuum Data: 5020.2 gms.  
% Recovery: 99.51 g 99.35 g SG = 0.9582 API = 16.2°

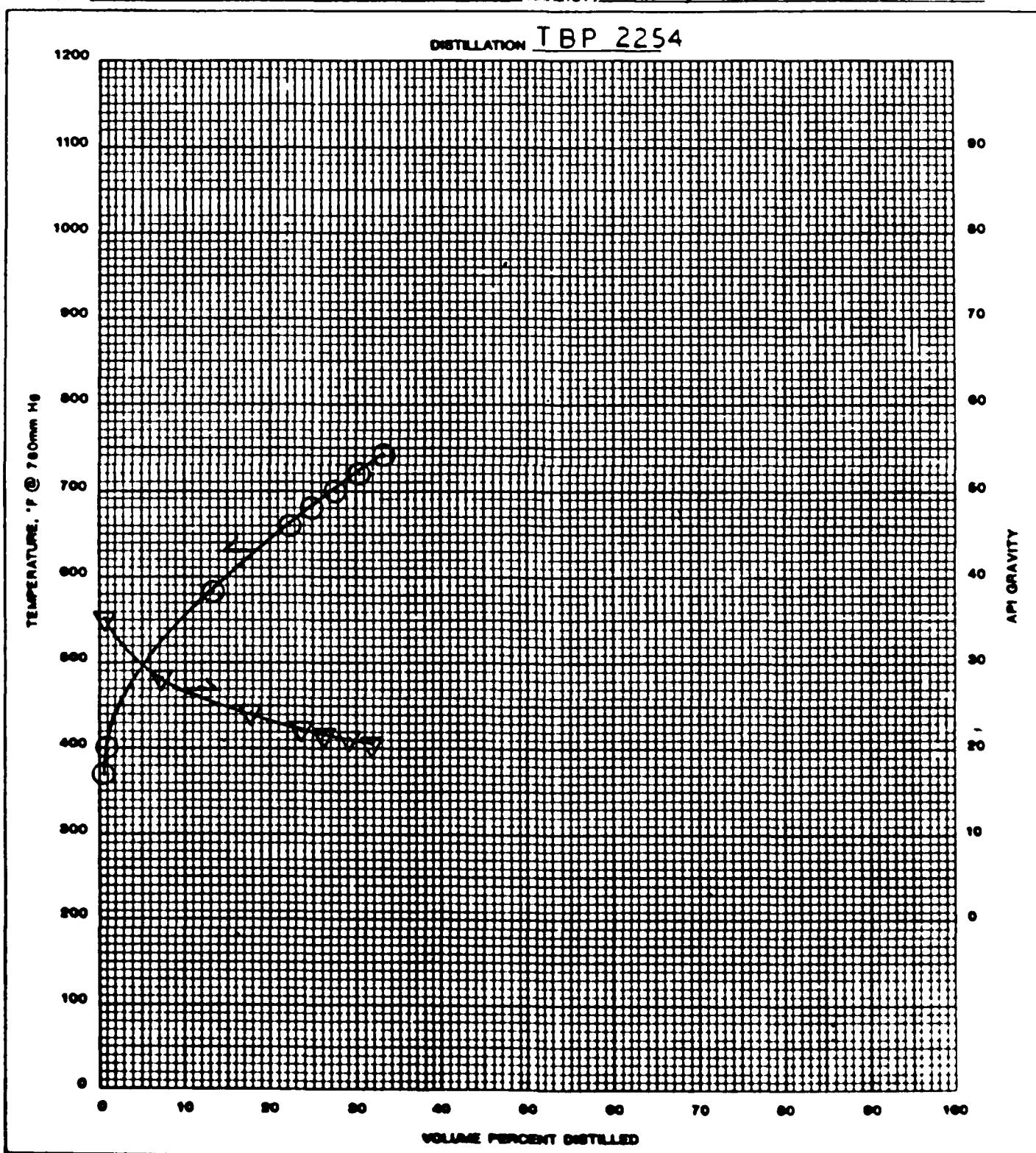
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6/21/85

SUBJECT: LAK CRUDE FROM SURTEK PAGE \_\_\_\_ OF \_\_\_\_

AUTHOR: \_\_\_\_\_ DATE: 5/3/85 PROJECT # \_\_\_\_\_

RF# 48125 ANALYST: C M Smith

DISTILLATION TBP 2254



DISTILLATION REPORT

Dist. Type: TBP  
 011 No. 36337  
 011 Source Alaskan North Slope Crude from the Avon Refinery

Cut Number	Dist. Range F at Atm.	Wt. (g)	Wt. (g)	# Weight %	Specific Gravity	*API	Vol. [ml]	Vol. %	Σ Vol. %
1	<.79(Cold Trap)	90.4	1.1	1.1	0.598	105.0	151.2	1.7	1.7
2	79-180	192.4	2.4	3.5	0.696	71.7	276.6	3.7	4.8
3	180-340	795.1	9.9	13.4	0.769	52.3	1034.1	11.5	16.3
4	340-380	204.5	2.5	15.9	0.801	45.1	255.5	2.8	19.1
5	380-480	653.1	8.1	24.0	0.832	38.4	785.1	8.7	27.8
6	480-520	345.3	4.3	28.3	0.856	33.6	403.3	4.5	32.3
7	520-650	1078.9	13.4	41.7	0.876	29.9	1231.1	13.7	46.0
8	650-750	826.3	10.3	52.0	0.902	25.3	916.6	10.2	56.2
9	750-950	1628.9	20.2	72.2	0.933	20.0	1734.3	19.4	75.6
10	950-1050	726.8	9.0	81.2	0.948	17.7	767.1	8.5	84.1
	Totals	6541.7	81.2				7566.3	84.1	
11	1050+	1516.3	18.8	100.0	1.026	6.3	1477.9	16.4	100.5
	Totals	8058.0					9044.2		
	340-520°F (kerosene)	1202.9	14.9	--	0.833	38.3	1443.9	16.0	

Charge: 8058.0 gms. 9001.0 mls. Charge Data: 8058.0 gms.  
 Recovery: 8058.0 gms. 9044.2 mls. SG = 0.896 API = 26.4°  
 L & H: 0.0 gms. (43.2) mls. Residuum Data: 1516.3 gms.  
 % Recovery: 100.0 % 100.5 % SG = 1.026 API = 6.3°

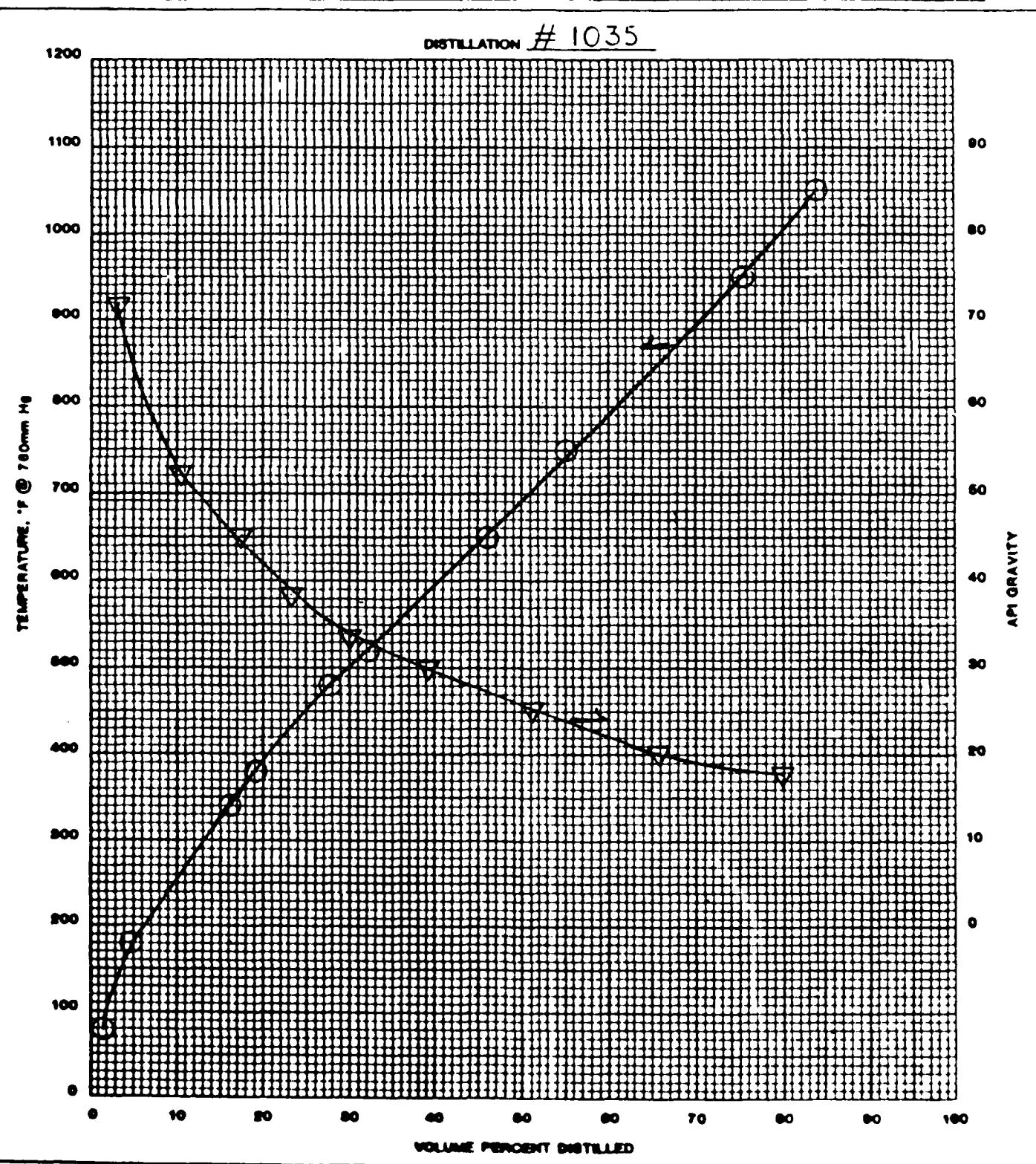
Disk CMS#1  
Doc TBPForm

SUBJECT: ALASKAN NORTH SLOPE CRUDE PAGE \_\_\_\_\_ OF \_\_\_\_\_

AUTHOR: \_\_\_\_\_ DATE: 3/31/82 PROJECT: \_\_\_\_\_

REF: 36337 ANALYST: RLH

DISTILLATION # 1035



**APPENDIX C**  
**HYDROTREATING AND SAMPLE PREP EQUIPMENT**

**J and A Associates, Inc.**

18200 West Highway 72

Golden, Colorado 80401

(303) 425-6021

**J & A HYDROTREATING/HYDROCRACKING CAPABILITIES**

Hydrotreating Equipment

We operate one hydrotreater pilot plant that contains two independent units in parallel. These units can be run as hydrotreater/hydrocracker, dual hydrotreaters, or linked together for larger scale hydrotreating. (See attached figure.)

**Reactor size:** Each reactor has a volume of 200 cc that can be decreased to 100 cc by internal spacers.

**Feed**

**Throughput:** For a single reactor, 40 to 400 cc of oil per hour may be fed. With both reactors in series, this rate can be doubled.

**Feed Type:**

We have run diesels, VGO's and coker gas oils. Resid processing may be possible depending upon resid quality.

**Pressure:**

Pressure vessels and reactors are rated at 3500 psig. Tubing and fittings are autoclave (20,000 psig). Normal operating pressure is 1350 psig.

**Temperature:**

Normal reactor temperature is 650-750°F, but substantially higher temperatures are obtainable. Heating is by external resistance coils. A cooling air circuit fine-tunes temperature control.

**Hydrogen Input:**

Gas cylinders are used in conjunction with a boost pump. A hydrogen recycle system is available, but is rarely used.

**Product Split:**

A high-pressure separator produces a purge gas stream which is metered and analyzed. Liquid product is depressurized, stabilized in a debutanizer tower, and metered and analyzed as vent gas and liquid product.

**Hydrocracker**

**Recycle:**

In the hydrocracker mode, product oil may be continuously fractionated at 400°F, and the 400°F+ recycled to extinction. This procedure limits fresh feed rate to about 60 cc per hour and requires extra time for line-out.

**Catalyst**

**Sulfiding:**

This is normally done with DMDS in diesel and requires as long as five days of continuous running.

**Test Runs:**

After sulfiding, feed is run for about four more days (24 hours per day) to stabilize yields. Then a 12 or 24 hour material balance test is performed, and run conditions are changed for subsequent tests. Each test at different conditions requires a line-out of one or two days.

**Hydrotreating/**

**Hydrocracking:** Normally, hydrocracking is a two stage operation, H/T being required to protect the H/C catalyst. By using both reactors simultaneously, this scheme may be used. Or, two H/T tests may be performed simultaneously, followed by two H/C tests after catalyst switching.

**Supporting Equipment**

**A. FCC pilot plant (ARCO LAB unit).**

This unit may be used to evaluate the hydrotreating of FCC feeds.

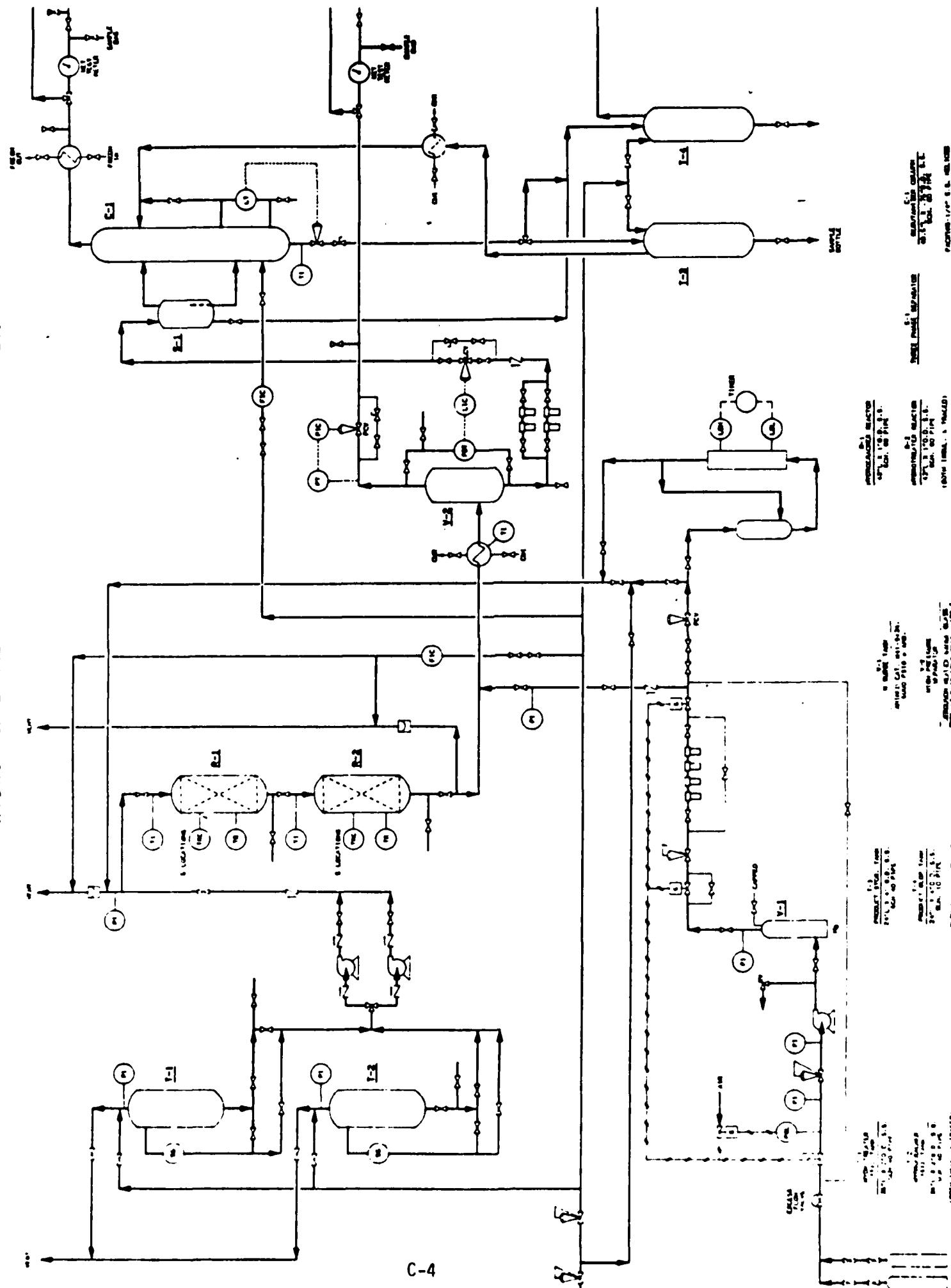
**B. Twenty-five gallon Batch Still and 5 gph Continuous Vacuum Still.**

These may be used to prepare feedstocks (up to 1050°F E.P.) from crudes or other refinery streams.

**C. Full analytical capabilities.**

Oils, gases and solids can be analyzed in-house by our well equipped laboratories.

## HYDROTREATER PILOT PLANT (REACTORS IN SERIES)



APPARATUS USED TO PREPARE  
HYDROTREATER FEEDSTOCK

( 25 GALLON BATCH STILL )

